

# CHEMICAL BONDING

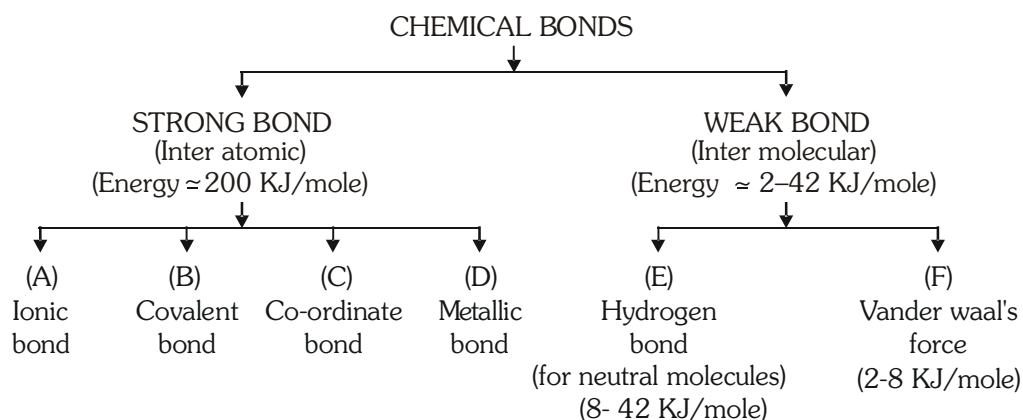
## 2.0 INTRODUCTION

- It is well known fact that except inert gases, no other element exists as independent atom under ordinary conditions.
- Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.
- A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

### Chemical Bond

- A force that acts between two or more atoms to hold them together as a stable molecule.
- It is union of two or more atoms involving redistribution of  $e^-$  among them.
- This process accompanied by decrease in energy.
- Decrease in potential energy (P.E.)  $\propto$  Strength of the bond.
- Therefore molecules are more stable than atoms.

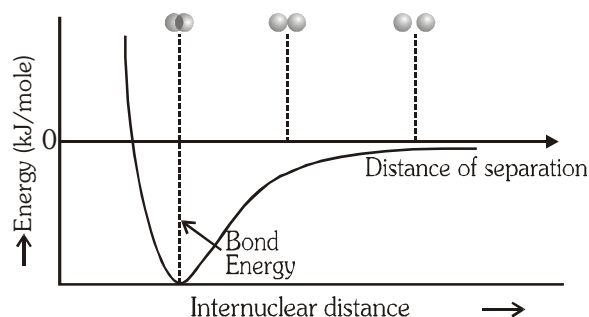
### Classification of Bonds



### Cause of Chemical Combination

#### (A) Tendency to acquire minimum energy

- When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.
- Two nuclei and electrons of both the atoms repels each other.
- If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- So Attraction  $\propto 1/\text{energy} \propto$  Stability.
- Bond formation is an exothermic process



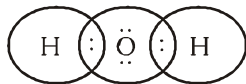
#### (B) Tendency to acquire noble gas configuration :

- Atom combines to acquire noble gas configuration.
- Only outermost electrons i.e.  $ns$ ,  $np$  and  $(n-1)d$  shells electrons participate in bond formation.
- Inert gas elements do not participate in bond formation, as they have stable electronic configuration hence will have minimum energy. (Stable configuration  $1s^2$  or  $ns^2np^6$ )

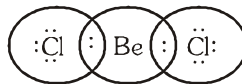


## 2.1 KOSSEL - LEWIS APPROACH TO CHEMICAL BONDING

- Every atom has a tendency to complete its octet in outermost shell
- H has the tendency to complete its duplet.
- To acquire inert gas configuration atoms lose or gain electron or share electron.
- The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obeys octet rule



Doesn't obey octet rule

### Exception of Octet Rule

#### (a) Incomplete octet molecules :- or (electron deficient molecules)

Compound in which octet is not complete in outer most orbit of central atom.

Example - Halides of IIIA groups,  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ , hydride of III A/ $13^{\text{th}}$  group etc.

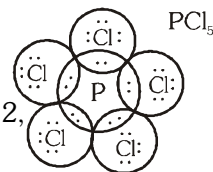


Other examples –  $\text{BeCl}_2$  ( $4e^-$ ),  $\text{HgCl}_2$  ( $4e^-$ ),  $\text{Ga}(\text{CH}_3)_3$  ( $6e^-$ )

#### (b) Expansion of octet or (electron efficient molecules)

Compound in which central atom has more than  $8e^-$  in outermost orbits.

**Example** - In  $\text{PCl}_5$ ,  $\text{SF}_6$  and  $\text{IF}_7$  the central atom P, S and I contain 10, 12, and 14 electrons respectively.



#### (c) Pseudo inert gas configuration :-

Cations which contain 18 electrons in outermost orbit

**Ex.**  $\text{Ga}^{+3}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Sn}^{+4}$ ,  $\text{Pb}^{+4}$  etc.

Electronic configuration of Ga -  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$

Electronic configuration of  $\text{Ga}^{+3}$  -  $1s^2, 2s^2, 2p^6, \underline{3s^2 3p^6 3d^{10}}$   
 $18e^-$

#### (d) Cations having electron between 9 to 17 in their outer most shell

**Ex.**  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Ti}^{+2}$  etc.

Electronic configuration of Fe -  $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$

Electronic configuration of  $\text{Fe}^{+3}$  -  $1s^2, 2s^2 2p^6, \underline{3s^2 3p^6 3d^5}$   
(less than  $18e^-$ )

#### (e) Odd electron molecules :-

Central atom have an unpaired electron or odd no ( $7e^-$ ,  $11e^-$  etc) of electrons in their outer most shell.

e.g. NO,  $\text{NO}_2$ ,  $\text{ClO}_2$  etc.



## VALENCY

It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

**Old concept :** Given by : **Frankland**

**Valency with respect to Hydrogen :** Valency of H = 1

It is defined as the number of hydrogen attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH <sub>2</sub>	AlH <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Valency	1	2	3	4	3	2	1

**Note :** Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

**Valency with respect to oxygen :** Valency of 'O' = 2

It is defined as twice the number of oxygen atoms attached with a particular atom.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
Valency	1	2	3	4	5	6	7

**Note :** Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

**New concept :** This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e<sup>-</sup> and from VA to zero group, it is –

$$[8 - (\text{number of valence } e^-)]$$

$$\text{Valency} = \text{No. of valence } e^-$$

$$\text{Valency} = (8 - \text{no. of valence } e^-)$$

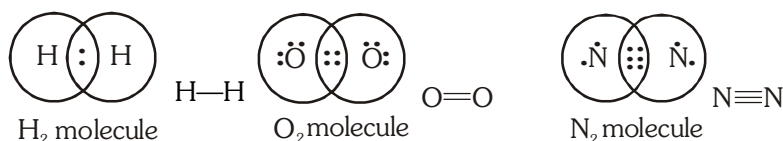
	↓				↓			
	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
	ns <sup>1</sup>	ns <sup>2</sup>	ns <sup>2</sup> np <sup>1</sup>	ns <sup>2</sup> np <sup>2</sup>	ns <sup>2</sup> np <sup>3</sup>	ns <sup>2</sup> np <sup>4</sup>	ns <sup>2</sup> np <sup>5</sup>	ns <sup>2</sup> np <sup>6</sup>
Valence shell e <sup>-</sup>	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0
					(8 - 5) = 3			(8 - 8) = 0

**Note :** All the elements of a group have same valencies because they have same number of valence shell electrons.



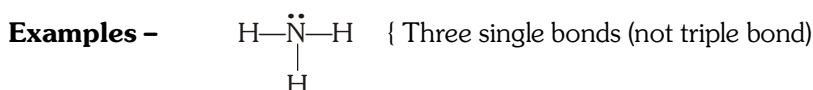
## 2.2 COVALENT BOND

- A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet)



- The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.
- Sharing of electrons may occurs in three ways –

No. of electrons shared between two atoms	Electron pair	Bond.
2	1	Single bond (—)
4	2	Double bond (=)
6	3	Triple bond (≡)



$\text{N}\equiv\text{N}$  Triple bond. (not three single bonds)  $\text{O}=\text{O}$  Double bond (Not two single bonds)  $\text{H}-\text{O}-\text{H}$  (Two single bonds.)

### Orbital Concept of Covalent Bond

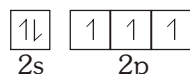
- One orbital can accommodate maximum 2 electrons with opposite spins like  $\boxed{\uparrow\downarrow}$
- Half filled orbital or unpaired electron orbital share one electron from another atom, to complete its orbital.
- Tendency to complete orbital or to pair the electron is an essential condition of covalent bond. Completion of octet is not the essential condition of covalent bond.
- Covalency** : It is the number of covalent bonds which an atom makes in a molecule.
- If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

## 2.3 VARIABLE VALENCY IN COVALENT BONDS

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
- The energy required for excitation of electrons is called promotion energy.
- Promotion rule – Excitation of electrons in the same orbit.

**Example –**

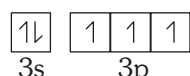
**(a) Nitrogen → Ground state**



Covalency 3 ( $\text{NCl}_3$ )

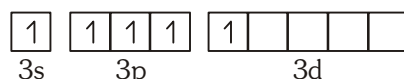
For Nitrogen → Excited states are not possible due to absence of vacant orbital that's why ( $\text{NCl}_5$ ) does not exist

**(b) Phosphorus → Ground state**



Covalency 3 ( $\text{PCl}_3$ )

Phosphorus → Excited state



Covalency – 5 ( $\text{PCl}_5$ )



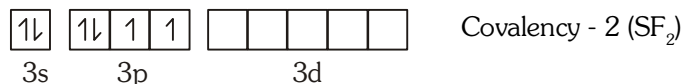
**Note :**

$\text{NCl}_3$  — exists

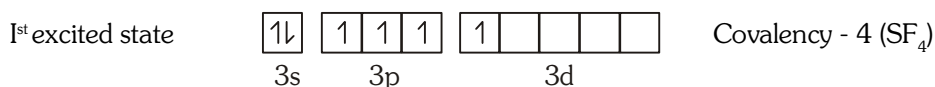
$\text{NCl}_5$  — doesn't exist (due to absence of d-orbitals in Nitrogen.) While  $\text{PCl}_3$  and  $\text{PCl}_5$  both exist because 3d orbitals are present in phosphorus.

$\text{OF}_2$  — exists, but  $\text{OF}_4$  and  $\text{OF}_6$  doesn't exist due to absence of d-orbitals While  $\text{SF}_4$  and  $\text{SF}_6$  exist due to presence of d-orbital which are present in its valence shell.

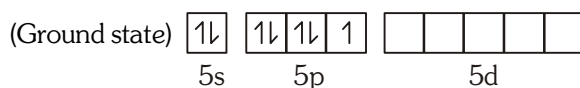
- It can explain existence of molecules.

**(c) Sulphur → Ground state.**

Sulphur → Excited state



So variable covalency of S is 2, 4, & 6.

**(d) Iodine has three lone pair of electrons**

So it shows three excited states – Maximum number of unpaired electrons = 7

Variable Valencies are 1, 3, 5 and 7

**2.4 CHARACTERISTIC OF COVALENT COMPOUND**

**(a) Physical state :-** Covalent compounds are found in all the three states - Gas, Solid & Liquid.

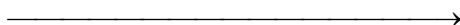
Separate molecules — In gaseous state

Associate molecules — In liquid & solid state

(Due to strong vander waal's force and hydrogen bonding among the molecules.)

As the molecular weight increases physical state changes -

eg. $\text{F}_2$ and $\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$ , $\text{At}_2$
gas	liquid	solid



Top to bottom in a group. Vander waal's force increases between the molecules.

**(b) Covalent solid :-** Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure.

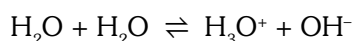
eg. Diamond, Graphite,  $\text{AlN}$ ,  $\text{SiC}$ ,  $\text{SiO}_2$  etc.

**Molecular solid :-** Discrete (separate) molecules are formed by covalent bonds and then the molecules associates due to intermolecular force of attraction. (van der Waal force)

eg. Solid  $\text{I}_2$ , dry ice (Solid  $\text{CO}_2$ ) etc.



- (c) **Conductivity :-** Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity. eg.  $\text{H}_2\text{O}$ , liq.  $\text{NH}_3$  etc.



Free ions are formed which can conduct electricity.

Exceptions :- Graphite,  $\text{HCl}$  in water.

- (d) **Solubility :-** Non polar compounds are soluble in non polar solvents. Non polar compounds forms vander waal bond with non polar solvent molecules.

Non polar solvents are  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$  etc.

- (e) **Isomerism :-** Covalent bond is rigid and directional, so it shows isomerism.

eg. Organic compounds.

- (f) **Reaction :-** Reaction between covalent compounds are slow. Because it involves breaking of old bonds and formation of new bonds.

### BEGINNER'S BOX-1

- Which condition favours the bond formation:  
(1) Maximum attraction and maximum potential energy  
(2) Minimum attraction and minimum potential energy  
(3) Minimum potential energy and maximum attraction  
(4) None of the above
- Which one of the following element will never obey octet rule:  
(1) Na (2) F (3) S (4) H
- Which is not an exception to octet rule ?  
(1)  $\text{BF}_3$  (2)  $\text{SiCl}_4$  (3)  $\text{BeI}_2$  (4)  $\text{ClO}_2$
- An oxide of chlorine which is an odd electron molecule is :  
(1)  $\text{ClO}_2$  (2)  $\text{Cl}_2\text{O}_6$  (3)  $\text{Cl}_2\text{O}_7$  (4)  $\text{Cl}_2\text{O}$

## 2.5 VALENCE BOND THEORY (VBT) :

- (A) It was presented by Heitler & London to explain how a covalent bond is formed.

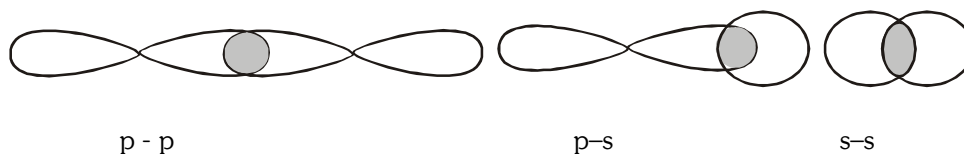
It was extended by Pauling & Slater.

- (B) The main points of theory are –

- To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
- Resulting bond acquires a pair of electrons with opposite spins to get stability.
- Orbitals come closer to each other from the direction in which there is maximum overlapping
- So covalent bond has directional character.
- Strength of covalent bond  $\propto$  extent of overlapping.
- Extent of overlapping depends on two factors.
  - Nature of orbitals – p, d and f are directional orbitals  $\rightarrow$  more overlapping  
s-orbital  $\rightarrow$  non directional – less overlapping



- (ii) Nature of overlapping – Co-axial overlapping - extent of overlapping more.  
 Collateral overlapping - extent of overlapping less  
 Order of strength of Co - axial overlapping –  $p - p > s - p > s - s$



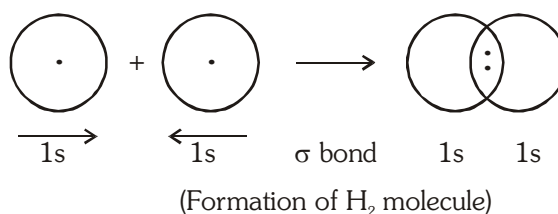
- (g) As the value of  $n$  increases, bond strength decreases.  
 $1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3$   
 $1s - 2p > 2s - 2p > 3s - 3p$
- (h) If  $n$  is same       $2p - 2p > 2s - 2p > 2s - 2s$
- (i) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.
- (j) This point can explain the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus etc.
- (k) Two types of bonds are formed on account of overlapping.  
 (A) Sigma ( $\sigma$ ) bond                      (B) Pi ( $\pi$ ) bond

### Sigma ( $\sigma$ ) Bond

- (a) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.
- (b)  $\sigma$  bond is directional.
- (c)  $\sigma$  bond do not take part in resonance.
- (d) Free rotation is possible about a single  $\sigma$  bond.
- (e) Maximum overlapping is possible between electron clouds and hence it is strong bond.
- (f) There can be only one  $\sigma$  bond between two atoms.

Sigma bonds are formed by four types of overlapping

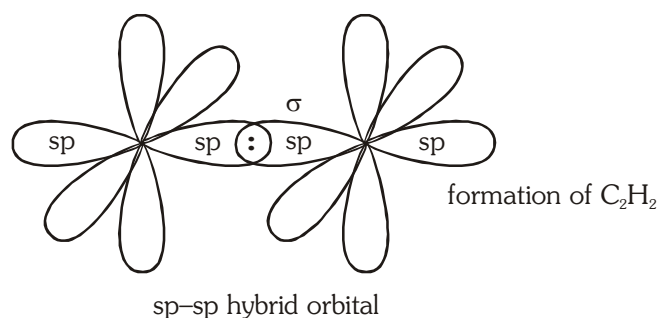
- (i) s - s overlapping – Two half filled s-orbitals overlap along the internuclear axis. Ex.  $H_2$  molecule.



- (ii) s - p overlapping (Formation of HF) – When half fill s-orbital of one atom overlap with half filled p-orbital of other atom.

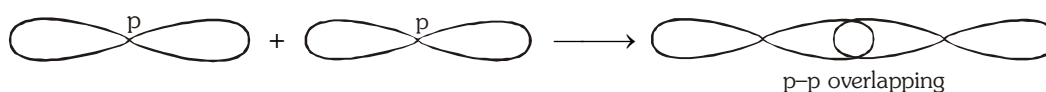


- (iii) Bond between two hybrid orbitals –  $sp^3 - sp^3$ ,  $sp^2 - sp^2$ ,  $sp^3 - sp^2$ ,  $sp^3 - sp$  etc.



**Note :** overlapping of hybrid orbitals form  $\sigma$  bond.

- (iv) p - p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different or same atoms.

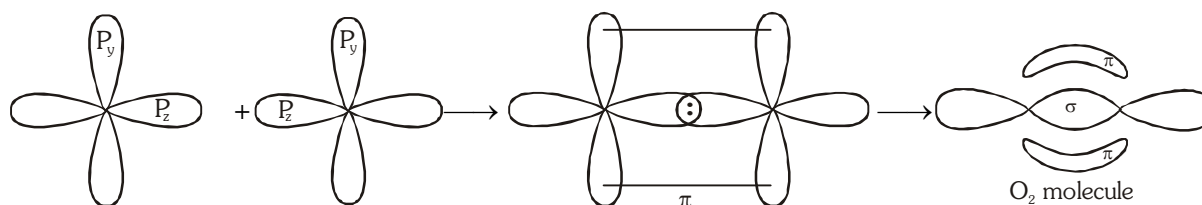


**Ex.** Formation of  $Cl_2$ ,  $F_2$ ,  $Br_2$

### Pi( $\pi$ )-Bond

- (a) The bond formed by sidewise (lateral) overlapping are known as  $\pi$  bonds.
- (b) Lateral overlapping is only partial, so formed are weaker and hence more reactive than  $\sigma$  bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for  $\pi$  bonds formation)

**Example –** Formation of  $O_2$  molecule –



**Note :** Only two orbitals of oxygen atom have unpaired  $e^-$  in each orbital for bonding.

Electron configuration of oxygen is –  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

- (c) Free rotation about a  $\pi$  bond is not possible.
- (d)  $\pi$  bond is weaker than  $\sigma$  bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)
- (e)  $\pi$  bonds are less directional, so do not determine the shape of a molecule.
- (f)  $\pi$  bond takes part in resonance.
- (g)  $\pi$  bond formed by pure or unhybrid orbitals.

### Comparison between $\sigma$ and $\pi$ bond

$\sigma$ bond	$\pi$ bond
1. Formed by axial overlapping	1. Formed by side by side overlapping
2. Involves s-s, s-p, p-p (axial) & hybrid orbitals	2. Involve p-p, p-d & d-d orbital
3. Extent of overlapping is more so stronger	3. Extent of overlapping is less so weaker
4. Free rotation around $\sigma$ bond is possible	4. Free rotation around $\pi$ bond is not possible
5. Hybridized or unhybridized orbital forms $\sigma$ bond	5. Hybridized orbital never forms $\pi$ bond
6. Independent existence of $\sigma$ -bond.	6. No independent existence.





## BEGINNER'S BOX-2

1. According to the valence bond theory, when a covalent bond is formed between two reacting atoms, the potential energy of the system becomes—  
 (1) negative                      (2) positive                      (3) minimum                      (4) maximum
2. The strongest covalent bond is formed by the overlap of— (If considering for same shell)  
 (1) *s* and *p* orbitals                      (2) *s* and *s* orbitals  
 (3) *p* and *d* orbitals                      (4) *p* and *p* collateral orbitals
3. In a triple bond there is sharing of :—  
 (1) 3-electrons                      (2) 4-electrons                      (3) Several electrons                      (4) 6-electrons
4. Which of the following configuration shows second excitation state of Iodine:—  
 (1) 

1↓	1↓	1	1	1				
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                      (2) 

1↓	1	1	1	1	1	1		
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 (3) 

1↓	1	1	1	1	1			
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                      (4) 

1	1	1	1	1	1	1		
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5. Variable covalency is exhibited by:—  
 (1) P and S                      (2) N and O                      (3) N and P                      (4) F and Cl
6. Which of the following bonds will have directional character  
 (1) Ionic bond                      (2) Metallic bond  
 (3) Covalent bond                      (4) Both covalent & metallic
7. Number of  $\sigma$  and  $\pi$  bonds present in  $\text{CH}_3 - \text{CH} = \text{CH} - \text{C} \equiv \text{CH}$  are -  
 (1) 10  $\sigma$ , 3 $\pi$                       (2) 10  $\sigma$ , 2 $\pi$                       (3) 9 $\sigma$ , 2 $\pi$                       (4) 8 $\sigma$ , 3 $\pi$
8. Which of the following statements regarding covalent bond is not true ?  
 (1) The electrons are shared between atoms  
 (2) The bond is non-directional  
 (3) The strength of the bond depends upon the extent of overlapping  
 (4) The bond formed may or may not be polar
9. Predict the nature of bond

Orbitals	Internuclear axis	Bond
$s + s$	any axis	.....
$s + p_x$	x-axis	.....
$s + p_y$	y-axis	.....
$s + p_z$	z-axis	.....
$p_x + p_x$	x-axis	.....
$p_y + p_y$	y-axis	.....
$p_z + p_z$	z-axis	.....
$p_x + p_y$	y or z-axis	.....
$p_y + p_z$	x or z axis	.....
$p_z + p_x$	x or y axis	.....



## 2.6 HYBRIDISATION

**Consider an example of Be compound :-**

If it is formed without hybridisation then  $\text{Cl} \overset{\text{p}-\text{s}}{\text{---}} \text{Be} \overset{\text{p}-\text{p}}{\text{---}} \text{Cl}$

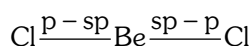
both the Be-Cl bonds should have different parameters and p-p bond strength > s-p bond strength. But practically bond strength and distance of both the Be-Cl bonds are same.

This problem may overcome if hybridisation of s and p-orbital occurs.

### Hybridisation

- (1) It is introduced by Pauling, to explain equivalent nature of covalent bonds in a molecule.
- (2) **Definition** : Mixing of different shape and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

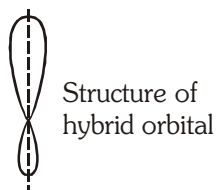
Now after considering s-p hybridisation in  $\text{BeCl}_2$



(Bond strength of both the bonds will be equal)

### Characteristic of Hybridisation

- (1) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.



- (2) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
- (3) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (4) The number of hybrid orbitals on central atom of a molecule or ion = number of  $\sigma$  bonds + lone pair of electron.
  - (i) The 1<sup>st</sup> bond between two atoms will be sigma.
  - (ii) The other bond between same two atoms will be pi bond.
  - (iii) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.
- (5) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp,  $\text{sp}^2$  and  $\text{sp}^3$  hybridisation in its compounds.
- (6) Hybrid orbitals are differentiated as sp,  $\text{sp}^2$ ,  $\text{sp}^3$  etc.
- (7) The repulsion between  $\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$
- (8) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.

$$\text{sp} < \text{sp}^2 < \text{sp}^3 < \text{sp}^3\text{d} < \text{sp}^3\text{d}^2 < \text{sp}^3\text{d}^3$$



## DETERMINATION OF HYBRIDISATION STATE

**Method (I) :** Number of hybrid orbital = number of  $\sigma$  bond + number of lone pair [surrounding the central atom]

**Method (II) :** To predict hybridisation following formulae may be used :

$$\text{No. of hybrid orbital} = \frac{1}{2} [\text{Ve}^- + \text{SA} \pm \text{C}]$$

[ $\text{Ve}^-$  = Total number of valence  $e^-$  in the central atom, SA = total number of monovalent atoms; C = charge]

**eg.**  $\text{NH}_4^+$   $\frac{1}{2} [5 + 4 - 1] = 4$   $\text{sp}^3$  hybridisation.

$\text{SF}_4$   $\frac{1}{2} [6 + 4] = 5$   $\text{sp}^3\text{d}$  hybridisation.

$\text{SO}_4^{2-}$   $\frac{1}{2} [6 + 2] = 4$   $\text{sp}^3$  hybridisation.

('O' is divalent so add only charge on anion)

$\text{NO}_3^-$   $\frac{1}{2} [5 + 1] = 3$   $\text{sp}^2$  hybridisation.

If such type of  $e^-$  pairs are –

two	–	$\text{sp}$	hybridisation
three	–	$\text{sp}^2$	hybridisation
four	–	$\text{sp}^3$	hybridisation
five	–	$\text{sp}^3\text{d}$	hybridisation
six	–	$\text{sp}^3\text{d}^2$	hybridisation
seven	–	$\text{sp}^3\text{d}^3$	hybridisation

S.No.	Formula	Total pair of $e^-$		Hybridisation	Geometry	Ex.
		bp	lp			
1.	$\text{AB}_2$	2	0	$\text{sp}$	Linear	$\text{BeCl}_2, \text{CO}_2$
2.	$\text{AB}_3$	3	0	$\text{sp}^2$	Trigonal Planar	$\text{BCl}_3, \text{BF}_3$
3.	$\text{AB}_4$	4	0	$\text{sp}^3$	Tetrahedral	$\text{CH}_4, \text{CCl}_4$
4.	$\text{AB}_5$	5	0	$\text{sp}^3\text{d}$	Trigonal bipyramidal	$\text{PCl}_5$
5.	$\text{AB}_6$	6	0	$\text{sp}^3\text{d}^2$	Octahedral (Square bipyramidal)	$\text{SF}_6$
6.	$\text{AB}_7$	7	0	$\text{sp}^3\text{d}^3$	Pentagonal bipyramidal	$\text{IF}_7$

### Position of lone pair & multiple bond

(i)  $\text{sp}/\text{sp}^2/\text{sp}^3$  = Any where

(ii)  $\text{sp}^3\text{d}$  = equatorial

(iii)  $\text{sp}^3\text{d}^2$  = axial (defined first)

(iv)  $\text{sp}^3\text{d}^3$   $\left\{ \begin{array}{l} \text{Lone pair} = 1 \text{ then equatorial} \\ \text{Lone pair} = 2 \text{ then axial} \end{array} \right.$

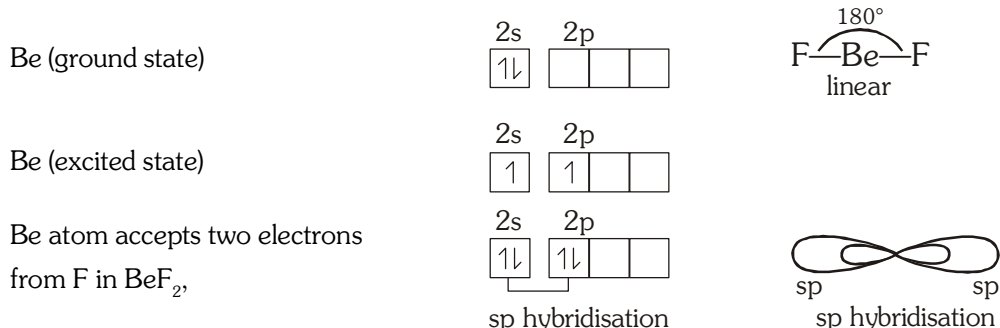
(v)  $\text{sp}^3\text{d}$  hybridisation      Axial bond length > equatorial bond length  
 $\text{sp}^3\text{d}^3$  hybridisation      Axial bond length < equatorial bond length       $\left. \vphantom{\begin{array}{l} \text{sp}^3\text{d} \\ \text{sp}^3\text{d}^3 \end{array}} \right\} \text{terminal atom same}$



## Types of Hybridisation

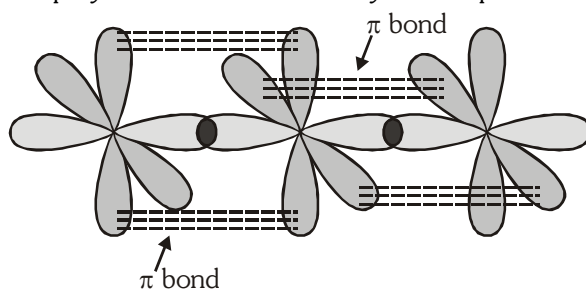
### (A) sp hybridisation :

- In this hybridisation one s- & one p- orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.
- These two sp hybrid orbitals are arranged in a straight line & at bond angle  $180^\circ$ .
- s-character 50%



### $\text{CO}_2$ Molecule ( $\text{O} = \text{C} = \text{O}$ ) :

In  $\text{CO}_2$  molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



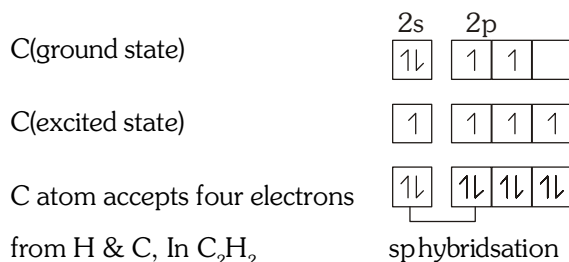
Molecular orbital picture of  $\text{CO}_2$

Thus,  $\text{CO}_2$  molecule is linear in shape & having  $180^\circ$  bond angle.

The bond length between C-O bond is reduced due to the presence of  $\pi$  bond.

### $\text{CH} \equiv \text{CH}$ [ $\text{H}-\text{C}_A \equiv \text{C}_B-\text{H}$ ]

In  $\text{CH} \equiv \text{CH}$  molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals

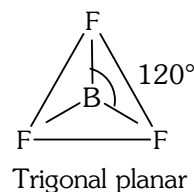
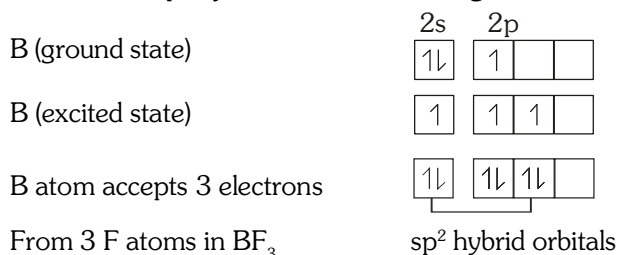


- sp hybrid orbital of each C overlaps to give sigma bond between C - C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C - H.
- The two unhybridised p orbitals of each C atom ( $p_y$  and  $p_x$ ) overlap laterally to form two  $\pi(\pi)$  bonds.
- Therefore in  $\text{H}-\text{C}_A \equiv \text{C}_B-\text{H}$ 
  - sigma bond between  $\text{C}_A - \text{C}_B$  is formed sp - sp overlapping
  - sigma bond between  $\text{C}_A - \text{H}$  is formed sp - s overlapping
  - sigma bond between  $\text{C}_B - \text{H}$  is formed sp - s overlapping
  - pi bond between  $\text{C}_A - \text{C}_B$  is formed :  $p_y - p_y$ ,  $p_x - p_x$  overlapping
- Each C atom forms two sigma bonds but in  $\text{C}_2\text{H}_2$ , total sigma bonds are 3
- Each C atom forms two  $\pi$  bonds. Total  $\pi$  bonds in  $\text{C}_2\text{H}_2$  are two
- Total number of bonds in acetylene are :  $3\sigma + 2\pi$  bond = 5 bonds.



**(B)  $sp^2$  Hybridisation :**

- (a) In this hybridisation one s & two p orbitals are mixed to give three new  $sp^2$  hybrid orbitals which are in same shape & equivalent energies.
- (b) These three  $sp^2$  hybrid orbitals are at angle of  $120^\circ$  & giving trigonal planar shape.

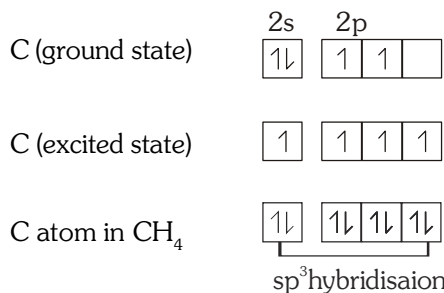


- (c) s - character 33.3 %

- $SnX_2$  having two  $\sigma$  bonds & one l.p. electron therefore hybridisation is  $sp^2$
- The bond angle in  $SnX_2$  will be less than  $120^\circ$  (due to presence of one l.p. $^e$ ).
- The shape of  $SnX_2$  molecule is bent.

**(C)  $sp^3$  Hybridisation :**

- (I) In this hybridisation one s orbital and three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as  $sp^3$  hybrid orbitals.
- (II) The angle between hybrid orbitals will be  $109^\circ 28'$  (6)



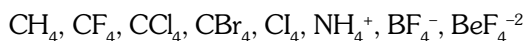
C atom share four electrons with four hydrogen atoms

- (III) The shape obtained from these hybrid orbitals would be tetrahedron.

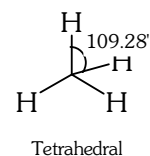
Three following examples represent this condition.

**(a) Four sigma bonds with zero lone pair electron :**

- (I) The following examples represent this condition.



- (II) In above compounds, bond angle is  $109^\circ 28'$  & tetrahedron shape.

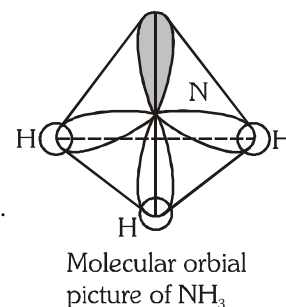
**(b) Three sigma bonds & one lone pair of electron :**

- (I) This condition is shown by following compounds & ions.



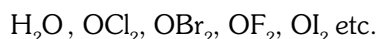
- (II)  $sp^3$  hybridisation, pyramidal shape & bond angle will be less than  $109^\circ 28'$ .

Due to the presence of one lone pair electron on nitrogen it repels bond pair electron more therefore bond angle reduced from  $109^\circ 28'$  to  $107^\circ$ . The repulsion between lp - bp > bp - bp.



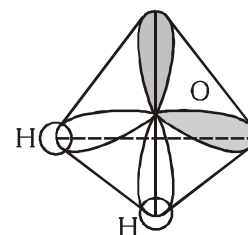
**(c) Two sigma bonds & two lone pair of electrons :**

(I) This condition is shown by following compounds and ions.



(II) In all above examples, the central atom showing  $\text{sp}^3$  hybridisation, angular shape and bond angle will be either less than  $109^\circ 28'$  or more than  $109^\circ 28'$ .

In  $\text{H}_2\text{O}$  the hybridisation on O atom is  $\text{sp}^3$ , but due to presence of two lone pair electrons they repel each other



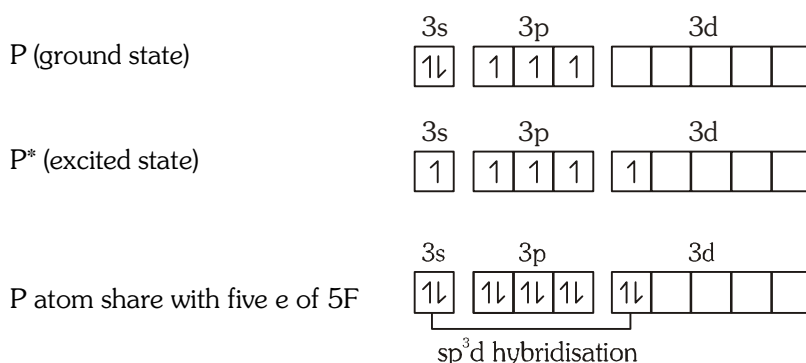
Molecular orbital picture of  $\text{H}_2\text{O}$

**(D)  $\text{sp}^3\text{d}$  Hybridisation :**

(I) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as  $\text{sp}^3\text{d}$  hybrid orbitals.

(II) Out of these five hybrid orbitals, three hybrid orbitals are at  $120^\circ$  angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes trigonal bipyramidal.

For example,  $\text{PF}_5$  showing  $\text{sp}^3\text{d}$  hybridisation



(III) In this hybridisation  $d_{z^2}$  orbital is hybridised with s and p orbitals.

In this way five  $\text{sp}^3\text{d}$  hybrid orbitals form five sigma bond with five F atoms and give a molecule of  $\text{PF}_5$ , shape of this molecule is trigonal bipyramidal.

Two axial P–Cl bonds are longer than three equatorial P–Cl bonds due to repulsion between 3 equatorial bp of  $e^-$  and 2 axial b.p. of  $e^-$

In above hybridisation, there are four conditions.

**(a) Five sigma bonds and zero lone pair electron :**

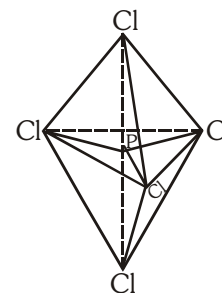
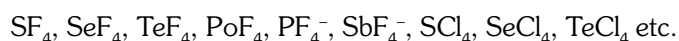
The following examples represent this conditions.



The shape of all the above molecules is trigonal bipyramidal.

**(b) Four sigma bonds and one lone pair of electron :**

The following examples represent this condition.

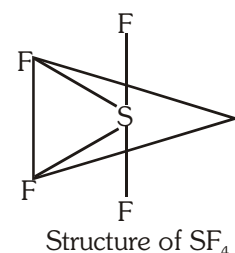
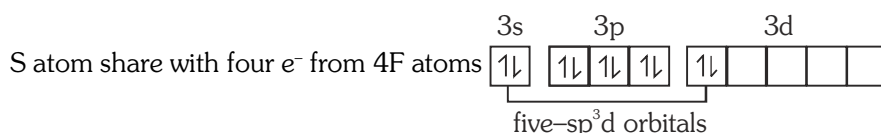


Structure of  $\text{PCl}_5$



The shape of all above examples will be irregular tetrahedron or See-saw

Example  $\text{SF}_4$

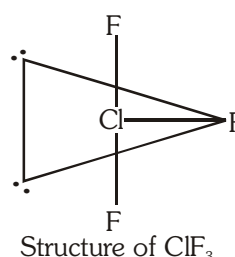


**(c) Three sigma bonds & two lone pair of electrons :**

The following examples represent this condition.

$\text{ClF}_3$ ,  $\text{BrF}_3$ ,  $\text{IF}_3$ ,  $\text{BrCl}_3$ ,  $\text{ICl}_3$  etc.

The shape of all above compounds is 'T' shape.



**(d) Two sigma bonds & three lone pair of electrons :**

The following examples represent this condition.

$\text{ICl}_2^-$ ,  $\text{IBr}_2^-$ ,  $\text{ClF}_2^-$ ,  $\text{IF}_2^-$ ,  $\text{BrF}_2^-$ ,  $\text{XeF}_2$ ,  $\text{I}_3^-$ ,  $\text{Br}_3^-$

The geometry of above examples will be linear shape.

**(E)  $sp^3d^2$  Hybridisation :**

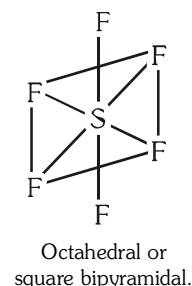
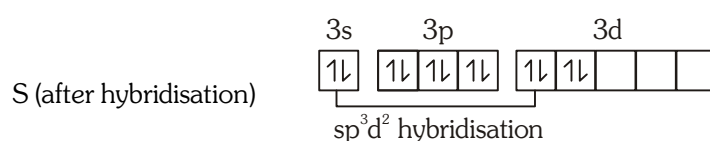
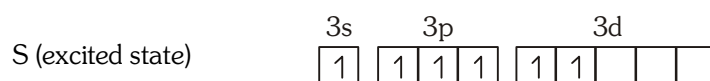
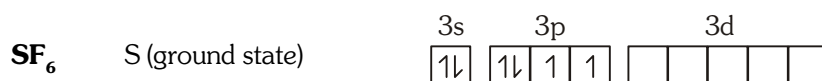
(I) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals ( $dz^2$ ,  $dx^2-y^2$ ) are mixed to give six new hybrid orbitals known as  $sp^3d^2$  hybrid orbitals.

(II) The geometry of molecule obtained from above six hybrid orbitals will be symmetrical octahedral or square bipyramidal.

(III) The angle between all hybrid orbitals will be  $90^\circ$ .

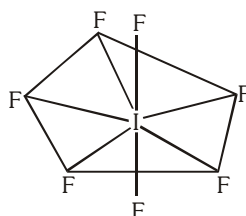
Example :  $\text{SF}_6$ ,  $\text{AlF}_6^{3-}$ ,  $\text{PF}_6^-$ ,  $\text{ICl}_5$ ,  $\text{XeF}_4$ ,  $\text{XeOF}_4$ ,  $\text{ICl}_4^-$ ,

(IV) Two 'd' orbital participates in the hybridisation are  $d_{x^2-y^2}$  and  $d_{z^2}$ .



**(F)  $sp^3d^3$  Hybridisation :**

- (I) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as  $sp^3d^3$  hybrid orbitals.
- (II) These seven  $sp^3d^3$  orbitals are configured in pentagonal bipyramidal shape.
- (III) Five bond angles are of  $72^\circ$  and 10 bond angles of  $90^\circ$ .
- (IV) The following examples showing  $sp^3d^3$  hybridisation –  $IF_7$  &  $XeF_6$ .

**(Pentagonal biipyramidal)****EXAMPLES ON  $sp^3d$  HYBRIDISATION**

Example	$\sigma$ bond	I.p.e.	Hybridisation	Bond angle	Shape
$PCl_5$	5	-	$sp^3d$	$120^\circ, 180^\circ$ & $90^\circ$	Trigonal bipyramidal
$SF_4$	4	1	$sp^3d$	$< 180^\circ, < 90^\circ, < 120^\circ$	Irregular tetrahedron
$ClF_3$	3	2	$sp^3d$	$87.6^\circ$	T-shape
$IF_3$	3	2	$sp^3d$	$87.6^\circ$	T-shape
$ICl_3$	3	2	$sp^3d$	$87.6^\circ$	T-shape
$Br_3^-$	2	3	$sp^3d$	$180^\circ$	Linear
$ICl_2^-$	2	3	$sp^3d$	$180^\circ$	Linear
$XeF_2$	2	3	$sp^3d$	$180^\circ$	Linear
$PCl_4^+$	4	-	$sp^3$		Tetrahedron
$NH_4^+$	4	-	$sp^3$		Tetrahedron
$NF_3$	3	1	$sp^3$		Pyramidal
$H_3O^+$	3	1	$sp^3$		Pyramidal
$SO_3^{2-}$	3	1	$sp^3$		Pyramidal
$XeO_3$	3	1	$sp^3$		Pyramidal
$H_2O$	2	2	$sp^3$		Angular (V)
$NH_2^-$	2	2	$sp^3$		Angular (V)
$OF_2$	2	2	$sp^3$		Angular (V)
$Cl_2O$	2	2	$sp^3$		Angular (V)
Diamond	4	-	$sp^3$		Tetrahedron
$SiO_2$	4	-	$sp^3$		Tetrahedron
$SiC$	4	-	$sp^3$		Tetrahedron
$NO_3^-$	3	-	$sp^2$	$120^\circ$	Trigonal planar
$SO_2$	2	1	$sp^2$	$< 120^\circ$	Angular (V)
$HCO_3^-$	3	-	$sp^2$	$120^\circ$	Trigonal planar
$SnCl_2$	2	1	$sp^2$	$< 120^\circ$	Angular (V)
$NO_2^+$	2	-	$sp$	$180^\circ$	Linear
$N_3^-$	2	-	$sp$	$180^\circ$	Linear

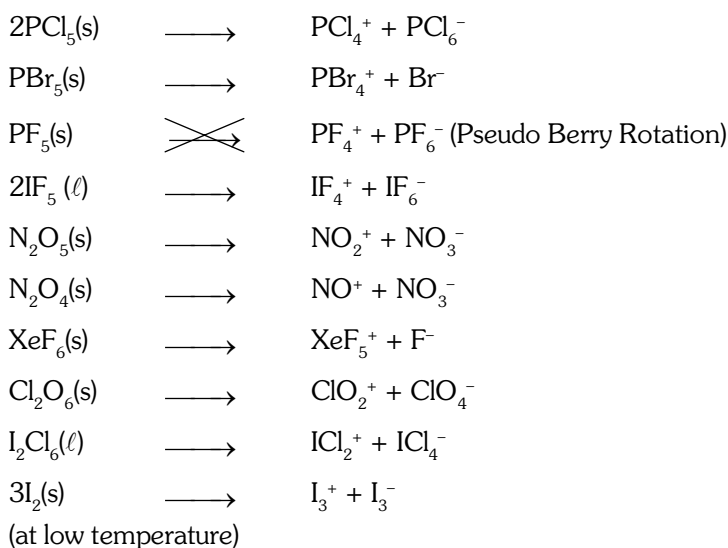


## BEGINNER'S BOX-3

1. Which of the following is incorrect about hybridization?
  - (1) The concept of hybridization is not applied to isolated atoms.
  - (2) Hybridization is the mixing of at least two non-equivalent atomic orbitals.
  - (3) The number of hybrid orbitals generated is more than the number of pure atomic orbitals that participate in the hybridization process.
  - (4) Hybridization requires an input of energy.
2. The hybridization state of the central atom in  $\text{HgCl}_2$  is—
  - (1)  $sp$
  - (2)  $sp^2$
  - (3)  $sp^3$
  - (4)  $dsp^2$
3. The hybridization state of the central atom in  $\text{AlI}_3$  is—
  - (1)  $dsp^2$
  - (2)  $sp^3$
  - (3)  $sp^2$
  - (4)  $sp$
4. In  $\text{C}_3\text{O}_2$ , the hybridization state of C is—
  - (1)  $sp^2$
  - (2)  $sp$
  - (3)  $sp^3$
  - (4)  $dsp^2$
5. By hybridization, we mean the hybridization of—
  - (1) electrons
  - (2) atomic orbitals
  - (3) atoms
  - (4) protons
6. The d- orbitals involved in  $sp^3d$  hybridisation is:-
  - (1)  $d_{x^2-y^2}$
  - (2)  $d_{z^2}$
  - (3)  $d_{xy}$
  - (4)  $d_{xz}$
7. A  $sp^3$  hybrid orbital contains:-
  - (1)  $\frac{3}{4}$  s- character
  - (2)  $\frac{1}{4}$  p - character
  - (3)  $\frac{3}{4}$  p - character
  - (4)  $\frac{1}{2}$  s - character
8. In the protonation of  $\text{NH}_3$  molecule, following statement is true:-
  - (1) A covalent bond is formed
  - (2) Hydrogen bond is formed
  - (3) Hybridisation state of N is changed
  - (4) Shape of  $\text{NH}_3$  molecule is changed
9. The shape of sulphate ion is :-
  - (1) Hexagonal
  - (2) Square planar
  - (3) Trigonal bipyramidal
  - (4) Tetrahedral
10. In which following compound, central atom has four bond pair and one lone pair:-
  - (1)  $\text{NH}_4^+$
  - (2)  $\text{ICl}_4^-$
  - (3)  $\text{SF}_4$
  - (4)  $\text{XeF}_4$
11. In which molecule s - p overlapping occurs ?
  - (1)  $\text{CH}_4$
  - (2)  $\text{NH}_3$
  - (3)  $\text{H}_2\text{O}$
  - (4) None of these

### Hybridisation in solid state :

- Compounds which change their structure in solid state/liquid state.



### Hybridisation in radicals :

Radical	hybridisation
CH <sub>3</sub>	.....
CF <sub>3</sub>	.....
ClO <sub>3</sub>	.....
NO <sub>2</sub>	.....

### Existence and Nonexistence :

Identify existing / non existing compounds / ions

- (a) PCl<sub>6</sub><sup>-</sup> (b) NH<sub>5</sub> (c) PH<sub>5</sub> (d) (CCl<sub>6</sub>)<sup>2-</sup> (e) (SiF<sub>6</sub>)<sup>2-</sup> (f) (SiCl<sub>6</sub>)<sup>2-</sup> (g) ClBr<sub>7</sub>  
(h) SH<sub>6</sub> (i) XeH<sub>4</sub> (j) XeOF<sub>4</sub> (k) FCl<sub>3</sub> (l) ClF<sub>3</sub> (m) BH<sub>4</sub><sup>-</sup> (n) (PI<sub>6</sub>)<sup>-</sup>

## 2.7 VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- (a) If the central atom possess only bonded pairs of electrons along with identical atoms then shape of the compound is symmetrical and according to Sidgwick & Powl.

eg.	BF <sub>3</sub>	—	120°	—	triangular
	CH <sub>4</sub>	—	109° 28'	—	tetrahedral
	CO <sub>2</sub>	—	180°	—	linear

- (b) If the central atom possess bonded pair of electrons as well as lone pair of electron, then shape of the molecule will be unsymmetrical ie. the original bond angle will disturbed due to repulsion between lone pair of electrons.

Similarly on having different type of side atoms, molecule becomes unsymmetrical due to unequal force of repulsion between e<sup>-</sup>. Order of repulsion is - [ℓp - ℓp > ℓp - bp > bp - bp]

$$\left[ \text{Bond angle} \propto \frac{1}{\text{Number of lone pair of electrons}} \right]$$

- (c) By increasing one lone pair of electron, bond angle is decreased approx by 2.5°.

eg.:-	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	→	sp <sup>3</sup>
	109°	107°	105°		hybridisation

## 2.8 BOND PARAMETERS

### Bond Length

The average distance between the nucleus of two atoms is known as bond length, normally it is represented in Å. eg. A — B

It depends mainly on electronegativities of constituent atoms.

**Case -I.** Electronegativity difference is zero then -

$$\text{Bond length} = r_A + r_B \quad \text{or} \quad d_{A-B} = r_A + r_B$$

where

$r_A$  = covalent radius of A

$r_B$  = covalent radius of B

$x_A$  = electronegativity of A

$x_B$  = electronegativity of B

If  $r_A = r_B$  then Bond length =  $2r_A$  or  $2r_B$

**Example :** - Cl - Cl

**Case - II** Electronegativity difference is not equal to zero then -

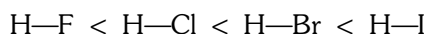
Bond length is given by Shomaker & Stevenson formula is - Bond length =  $r_A + r_B - 0.09 (x_A - x_B) \text{Å}$

$(x_A - x_B)$  = Difference in electronegativities



## Factors Affecting Bond Length

(a) **Δ electronegativity** :- Bond length  $\propto \frac{1}{\Delta EN}$  (While B.E.  $\propto \Delta EN$ )



(b) **Bond order or number of bonds** :- Bond length  $\propto \frac{1}{\text{Number of bonds or bond order}}$

Bond energy  $\propto$  Number of bond

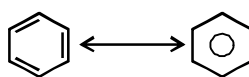
ex.	C—C,	C = C,	C $\equiv$ C	
Bond length	1.54 Å	1.34 Å	1.20 Å	← increasing
Bond energy	80	140	180-200 K.Cal.	increasing →
	C—O	C = O	C $\equiv$ O	
	1.43 Å	1.20 Å	1.13 Å	
			C $\equiv$ N	
	1.47 Å	1.28 Å	1.15 Å	

(c) **Resonance** :- Due to resonance bond length affected

Ex.1. Benzene

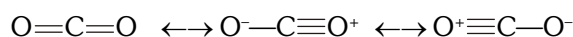
C—C bond length 1.54 Å

C=C bond length 1.34 Å



But bond length is between single and double bond is = 1.39 Å

Ex.2. Bond length of C—O in CO<sub>2</sub> is 1.15 Å Resonance occurs in CO<sub>2</sub> is as follows -



Bond length = 1.15 Å (Between double & triple bond)

(d) **Hybridization** : - Bond length  $\propto \frac{1}{s \text{ character}}$

Example :-

s-character increases ↓

Compound	Hybridisation	Bond length
Ethane	sp <sup>3</sup> — sp <sup>3</sup>	1.54 Å
	sp <sup>3</sup> — sp <sup>2</sup>	1.51 Å
	sp <sup>3</sup> — sp	1.47 Å
C=C—C=C	sp <sup>2</sup> — sp <sup>2</sup>	1.46 Å
C=C—C≡C	sp <sup>2</sup> — sp	1.42 Å
C≡C—C≡C	sp — sp	1.37 Å

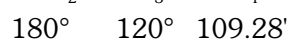
## Bond Angle

The minimum angle between any two adjacent bonds is known as bond angle.

It is represented in degree (°), min (') and second (")

**Factors affecting the bond angle -**

**Step I : Hybridisation or % 's' character :** Bond angle  $\propto$  % s character



## Step II : Lone pair

When hybridisation is same, lone pair are different.

$$\text{Bond angle} \propto \frac{1}{\text{No. of lone pair}}$$

**Example :-**

	$\text{CH}_4$	$\ddot{\text{N}}\text{H}_3$	$\text{H}_2\ddot{\text{O}}:$
Hybridisation	$\text{sp}^3$	$\text{sp}^3$	$\text{sp}^3$
Bond angle	$109^\circ$	$107^\circ$	$105^\circ$
	No l.p.	one l.p.	two l.p.

- In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

## Step III : Central Atom

$$\text{Bond angle} \propto \text{Electronegativity of central atom}$$

In  $\text{AB}_x$  type of molecules if side atoms are same and EN of central atom increases the bond angle increases.



- Electronegativity of 'O' > Electronegativity of 'S'
- Bond angle of  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

**Example :-**

	$\ddot{\text{N}}\text{H}_3$	$\ddot{\text{P}}\text{H}_3$	$\ddot{\text{As}}\text{H}_3$
Bond angle	$107^\circ$	$93^\circ$	$91^\circ$

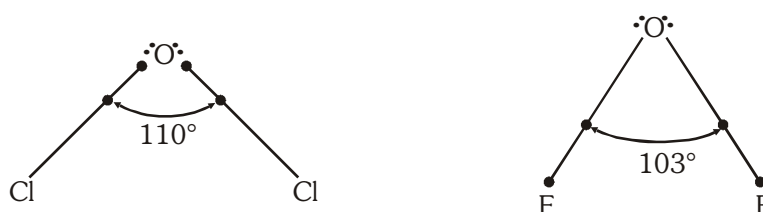
→

- Electronegativity decreasing.  
- Bond angle will decrease

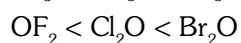
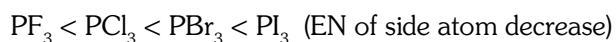
## Step IV : Side atom

$$\text{Bond angle} \propto \frac{1}{\text{electronegativity of bonded atom}} \propto \text{size of side atom}$$

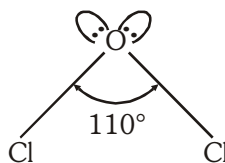
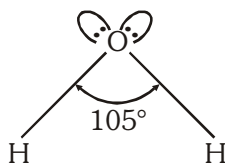
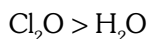
In  $\text{AB}_x$  type molecules, if central atoms are same and the EN of side atoms increases then bond angle decreases.



Electronegativity of Fluorine is greater than chlorine



Bond angle depends on size of side atom, On increasing size of side atom bond angle increases.



When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

$\text{sp}^3$	$\text{OF}_2$	103 - 105°	Electronegativity of bonded atom is decreasing ↓
$\text{sp}^3$	$\text{Cl}_2\text{O}$	109 - 111°	
$\text{sp}^3$	$\text{Br}_2\text{O}$	116 - 118°	

### Bond Energy (BE)

Bond energy may be defined as -

- Bond formation energy :- Energy released when any bond is formed is known as bond formation energy or bond energy.
- Bond dissociation energy :- Energy required to dissociate any bond is known as Bond dissociation energy.

Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

**Case-I** In diatomic molecule :

Bond energy = bond dissociation energy

**Example:-**  $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{F}_2$

**Case-II** For polyatomic molecule :-

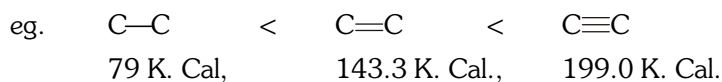
Bond energy  $\simeq$  Bond dissociation energy (D)

### Factors Affecting The Bond Energy

- |                                |                   |                        |                   |
|--------------------------------|-------------------|------------------------|-------------------|
| (a) $\Delta$ Electronegativity | (b) Bond order    | (c) Atomic size        | (d) Bond polarity |
| (e) Resonance                  | (f) Hybridisation | (g) Lone pair electron |                   |

**(a)  $\Delta$  Electronegativity :-** Bond energy  $\propto \Delta \text{EN}$  eg.  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

**(b) Bond order :-** Bond energy  $\propto$  Bond order.



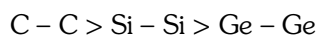
**(c) Atomic size :-** Bond energy  $\propto \frac{1}{\text{Atomic size}}$  eg.  $\text{C}\equiv\text{C} < \text{C}\equiv\text{N} < \text{N}\equiv\text{N}$

**Exception :-** In case of halogen group, order of bond energy is -

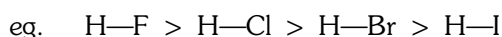


Because of higher electron density and small size of F atoms, repulsion between electrons of two F atoms, weakens the bond energy.

Other example  $\text{S}-\text{S} > \text{O}-\text{O}$



**(d) Bond Polarity :-** Bond energy  $\propto$  Bond polarity



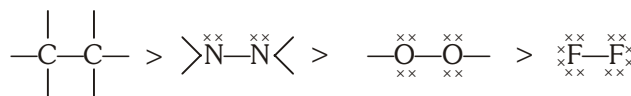
(e) **Resonance** :- Bond energy increases due to resonance.

eg. In benzene bond energy of C—C increases due to  $\pi$  electrons of C = C.

(f) **Hybridisation** :- Bond energy  $\propto$  s-character in hybrid orbitals.

eg.  $sp-sp > sp^2-sp^2 > sp^3-sp^3$   
s.character - 50 %      33.3 %      25 %

(g) **Lone pair of electrons** :- Bond energy  $\propto \frac{1}{\text{lone pair of electrons}}$



Size of F and O atoms are small so their bond energy should be high (small atomic radius) but it is actually less, due to lone pair of electrons present on F and O atoms, which repels each other in F—F and —O—O—type of bonds.

**Important Note (Summary) :**

(i) Bond strength  $\propto$  overlapping (if orbitals are given)

(ii) Bond strength  $\propto \frac{1}{\text{size of orbitals}}$

e.g.  $1s-2p > 1s-3p > 1s-4p$

(iii) If orbitals are of same shell

Bond strength  $\propto$  extent of overlapping  $\propto$  directional properties

$2p-2p > 2s-2p > 2s-2s > 2p-2p$  (Side ways)

Axial overlap

(iv)  $\pi$ -bond strength

$2p\pi-2p\pi > 2p\pi-3d\pi > 2p\pi-3p\pi > 3p\pi-3p\pi$

(v) O = O exist but S = S does not exist at room temperature.

(vi) N  $\equiv$  N exist but P  $\equiv$  P does not exist at room temperature.

(vii) O=C=O exist but O=Si=O does not exist.

#### BEGINNER'S BOX-4

- Which of the following molecules has the longest nitrogen-nitrogen bond?  
 (1)  $N_2H_4$  (2)  $N_2$   
 (3)  $N_2F_2$  (4) All have equal bond lengths
- Which of the following molecules has the highest value of carbon-carbon bond energy?  
 (1)  $C_2H_4$  (2)  $C_3H_8$  (3)  $C_2H_2$  (4)  $C_2H_6$
- Which of the following has the shortest bond length?  
 (1)  $Br_2$  (2)  $F_2$  (3)  $Cl_2$  (4)  $I_2$
- In ethene, the carbon-carbon bond distance is—  
 (1) 154 pm (2) 120 pm (3) 134 pm (4) 142 pm
- Carbon-halogen bond is strongest in the following  
 (1)  $CH_3Cl$  (2)  $CH_3Br$  (3)  $CH_3F$  (4)  $CH_3I$
- The correct order of bond length is  
 (1)  $C-C < C=C < C\equiv C$  (2)  $C\equiv C < C=C < C-C$   
 (3)  $C=C < C\equiv C < C-C$  (4)  $C=C < C-C < C\equiv C$
- The F—F bond is weak because :  
 (1) The repulsion between the nonbonding pairs of electrons of two fluorine atoms is large  
 (2) The ionization energy of the fluorine atom is very low  
 (3) The length of the F—F bond much larger than the bond lengths in other halogen molecules  
 (4) The F—F bond distance is small and hence the internuclear repulsion between the two F atoms is very low
- The correct order of decreasing bond energy is:-  
 (1)  $O-O > S-S > Se-Se$  (2)  $C-C > Si-Si > Ge-Ge$   
 (3)  $F-F > O-O > N-N$  (4)  $F-F > Cl-Cl > Br-Br$



9. The bond length does not affected by:-  
 (1) Electron affinity (2) Bond order (3) Hybridisation (4) Resonance
10. In allene structure three carbon atoms are joined by :  
 (1) Three sigma bonds and three pi bonds (2) Two sigma bonds and one pi bond  
 (3) Two sigma bonds and two pi bonds (4) Three pi bonds only

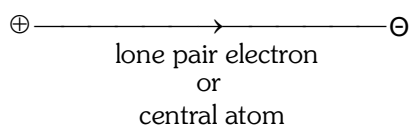
## 2.9 DIPOLE MOMENT

### POLARITY OF BOND (IONIC NATURE IN COVALENT BOND)

- (a) Polarity of any polar covalent bond or molecule is measured in terms of dipole moment.  
 (b) For measurement of extent of polarity, Pauling introduced the concept of dipole moment ( $\mu$ ).  
 The product of positive or negative charge ( $q$ ) and the distance ( $d$ ) between two poles is called dipole moment.

Here -  $\mu = q \times d$  (magnitude of charge  $\times$  distance),

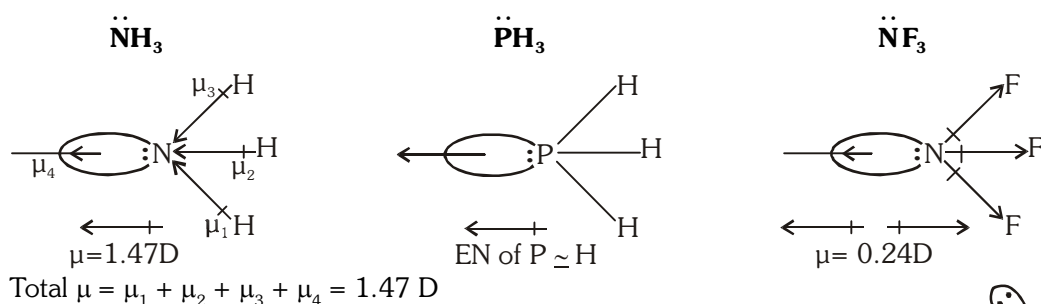
- (c) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.  
 (d) Direction of dipole moment is represented by an arrow pointing from electro +ve to electro -ve element and from central atom to lone pair of electrons.



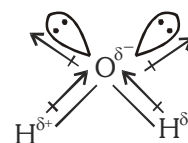
- (e) Unit of dipole moment is Debye  
 $1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm} = 3.33 \times 10^{-30} \text{ coulomb metre}$
- (f) In the diatomic molecule  $\mu$  depends upon difference of EN i.e.  $\mu \propto \Delta \text{EN}$   
 order of  $\mu$ ,  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$   
 $\mu = 0$  for  $\text{H-H}$ ,  $\text{F-F}$ ,  $\text{Cl-Cl}$ ,  $\text{Br-Br}$ ,  $\text{O-O}$
- (g) For polyatomic molecules  $\mu$  depends on the vector sum of dipole moments of all the covalent bonds.  
 (h) For  $\text{PCl}_5$  and  $\text{SF}_6$ , etc.  $\mu = 0$  due to their symmetrical geometry (According to charge).  
 (i) Benzene, naphthalene, diphenyl have  $\mu = 0$  due to planar structure.  
 (j) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual  $\mu$  of every bond should be zero).

**Example -**  $\text{BX}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{PCl}_5$ ,  $\text{SiH}_4$  etc.

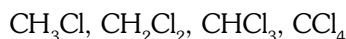
In these examples the bond B-F, C-Cl, C-H, C-O, P-Cl etc. are polar even though compounds are non-polar.



- (k) Dipole moment of  $\text{H}_2\text{O}$  is 1.85 D which is resultant  $\mu$  of two O-H bonds.  
 $\mu$  of  $\text{H}_2\text{O} > \mu$  of  $\text{H}_2\text{S}$  because electronegativity of oxygen is higher than sulphur.
- (l) Angular structure of molecule have greater dipole moment.



**Ex.** Write the order of the dipole moment of following compounds ?



**Sol.** Right order is  $\longrightarrow \text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2 < \text{CH}_3\text{Cl}$   
 $\mu = 0 \qquad 1.02 \qquad 1.55 \qquad 1.93$

### Applications of Dipole Moment

**(a) To determine polarity and geometry of molecule :-**

If  $\mu = 0$  compound is non polar and symmetrical

eg.  $\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_4$ ,  $\text{BeF}_2$  etc.

If  $\mu \neq 0$  compound will be polar and unsymmetrical.

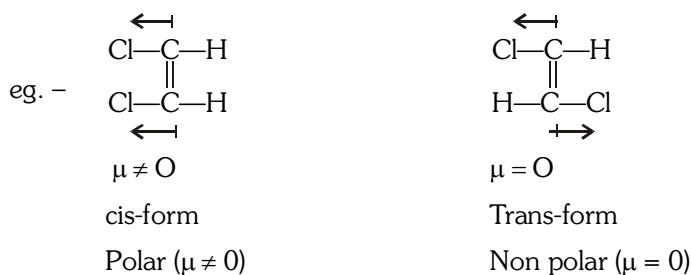
$\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  etc.

**(b) To calculate % ionic character :-**

$$\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical Value of } \mu} \times 100$$

**(c) To distinguish cis form or trans form :-**

(I) Dipole moment of cis isomers is normally higher than trans isomers.



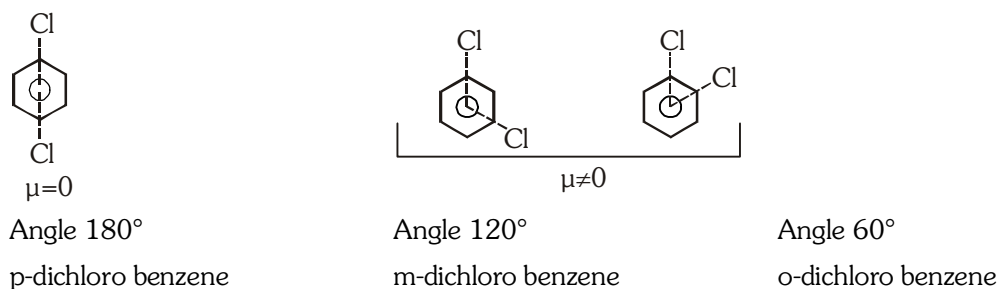
(II) If two groups have opposite inductive effect then trans-isomer will have greater dipole moment.



**(d) To locate position of substituents in aromatic compounds.**

$$\mu \propto \frac{1}{\text{Bond angle}}$$

(I) If same substituents are present in the symmetrical position  $\mu$  of benzene ring compounds will be zero.



(II) As angle between vector decreases value of  $\mu$  increases.





## Illustrations

**Illustration 1.** Calculate the  $\mu$  of HCl ? If bond distance is  $1.34 \text{ \AA}$ , charge =  $4.8 \times 10^{-10}$  esu and calculate % ionic character if experimental value of  $\mu = 1.08 \text{ D}$  ?

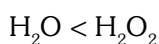
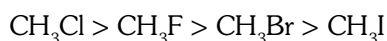
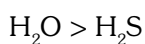
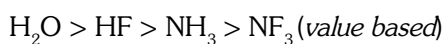
**Solution**  $\mu = q \times d = 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$

$$\mu = 6.4 \times 10^{-18} \text{ esu cm.}$$

$$\% \text{ Ionic character} = \frac{1.08 \times 10^{-18}}{6.4 \times 10^{-18}} \times 100 = 16.79 \%$$

### GOLDEN KEY POINTS

● **Some important orders of dipole moments :**



### BEGINNER'S BOX-5

1. Which of the following contains polar and nonpolar bonds?  
 (1)  $\text{H}_2\text{O}_2$                       (2)  $\text{CH}_4$                       (3)  $\text{HCN}$                       (4)  $\text{NH}_4\text{Cl}$
2. Carbon tetrachloride has no net dipole moment because of–  
 (1) Similar electron affinity of C and Cl                      (2) its regular tetrahedral geometry  
 (3) its planar geometry                      (4) similar sizes of C and Cl atoms
3. Which of the following molecules is nonpolar?  
 (i)  $\text{PbCl}_4$                       (ii)  $\text{BF}_3$                       (iii)  $\text{SnCl}_2$                       (iv)  $\text{CS}_2$   
 (1) (i), (ii), (iii)                      (2) (i), (ii), (iii), (iv)                      (3) (i), (ii), (iv)                      (4) (ii), (iii), (iv)
4. Which of the following has the highest dipole moment ?  
 (1) *o*-Dichlorobenzene    (2) *m*-Dichlorobenzene    (3) *p*-Dichlorobenzene    (4) All have equal values
5. Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contain polar covalent bonds but  $\text{CO}_2$  is nonpolar while  $\text{H}_2\text{O}$  is polar because–  
 (1) H atom is smaller than C atom  
 (2)  $\text{CO}_2$  is a linear molecule while  $\text{H}_2\text{O}$  is an angular molecule  
 (3) O – H bond is more polar than C – H bond  
 (4)  $\text{CO}_2$  contains multiple bonds while  $\text{H}_2\text{O}$  has only single bonds



## 2.10 MOLECULAR ORBITAL THEORY (MOT)

MOT put forward by Hund & Mulliken, which can be applied to explain the properties, which the old VBT (Valence bond theory) was unable to explain. eg. Paramagnetic nature of  $O_2$  molecule, as per VBT ( $:O = O:$ ) it should be diamagnetic.

**Definition** : The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

### Characteristic of Molecular Orbitals

- Molecular orbital formed by overlapping of atomic orbital of same energy.
- Number of molecular orbital formed = number of atomic orbitals involved in overlapping.
- Half of the molecular orbital have lower energy are called Bonding molecular orbital.
- Half are of higher energy - termed as Antibonding molecular orbital.
- Electronic configuration in various molecular orbital are governed by same three rules.
  - (1) Aufbau's rule
  - (2) Hund's rule
  - (3) Pauli's exclusion principle.
- Wave function for bonding molecular orbital is  $\psi_b = \psi_A + \psi_B$
- Wave function for antibonding molecular orbital is  $\psi_a = \psi_A - \psi_B$   
 $\psi_A$  = wave function of atom A  
 $\psi_B$  = wave function of atom B

### Comparison of Bonding molecular orbital & Antibonding molecular orbital:

Bonding molecular orbital(BMO)	Antibonding molecular orbital (ABMO)
1. Bonding MO is the result of the linear combination of AO when their wave function are added $\psi_b = \psi_A + \psi_B$	1. ABMO is result of linear combination of AO when their wave function are subtracted $\psi_a = \psi_A - \psi_B$
2. Generally it does not have nodal plane.	2. It always have a nodal plane between two nuclei of bonded atom.
3. Electron density increases between two nuclei resulting attraction between two atoms.	3. Electron density decreases in between two nuclei, leads to repulsion between two atoms.
4. Energy of BMO is less, hence stable.	4. Energy of ABMO is high.
5. Electron placed in a BMO stabilises a molecule.	5. Electron placed in the ABMO destabilises the molecule.

### Notation of molecular orbitals

As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital

For bonding molecular orbital -  $\sigma, \pi$  etc.

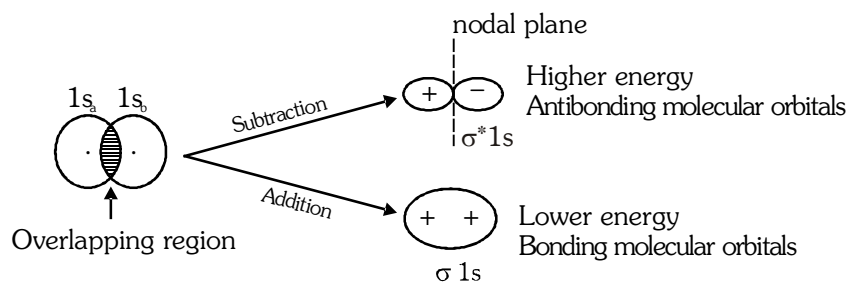
For antibonding molecular orbital-  $\sigma^*, \pi^*$  etc.

are used for different shapes of electron cloud.

### Shapes of Molecular Orbitals (L.C.A.O. Method)

(A) ( $\sigma$  molecular orbital) :- It is formed by two ways -

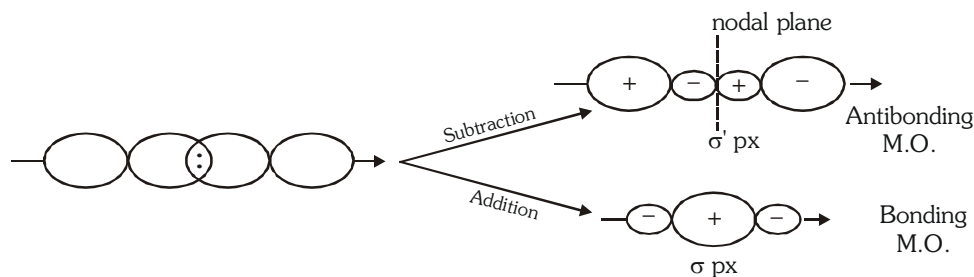
- Combination of s-orbitals -



- $\sigma^* 1s$  have one nodal plane

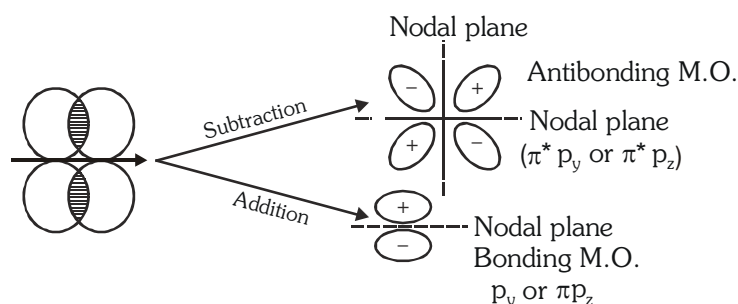


(b) End on overlapping of p-orbitals - (Linearly) :-



●  $\sigma^* p_x$  have one nodal plane

### (B) $\pi$ (pi) molecular orbitals :-



Positive sign, represent maximum probability finding of electrons.

$\pi^* p_y$  or  $\pi^* p_z$  have two nodal plane

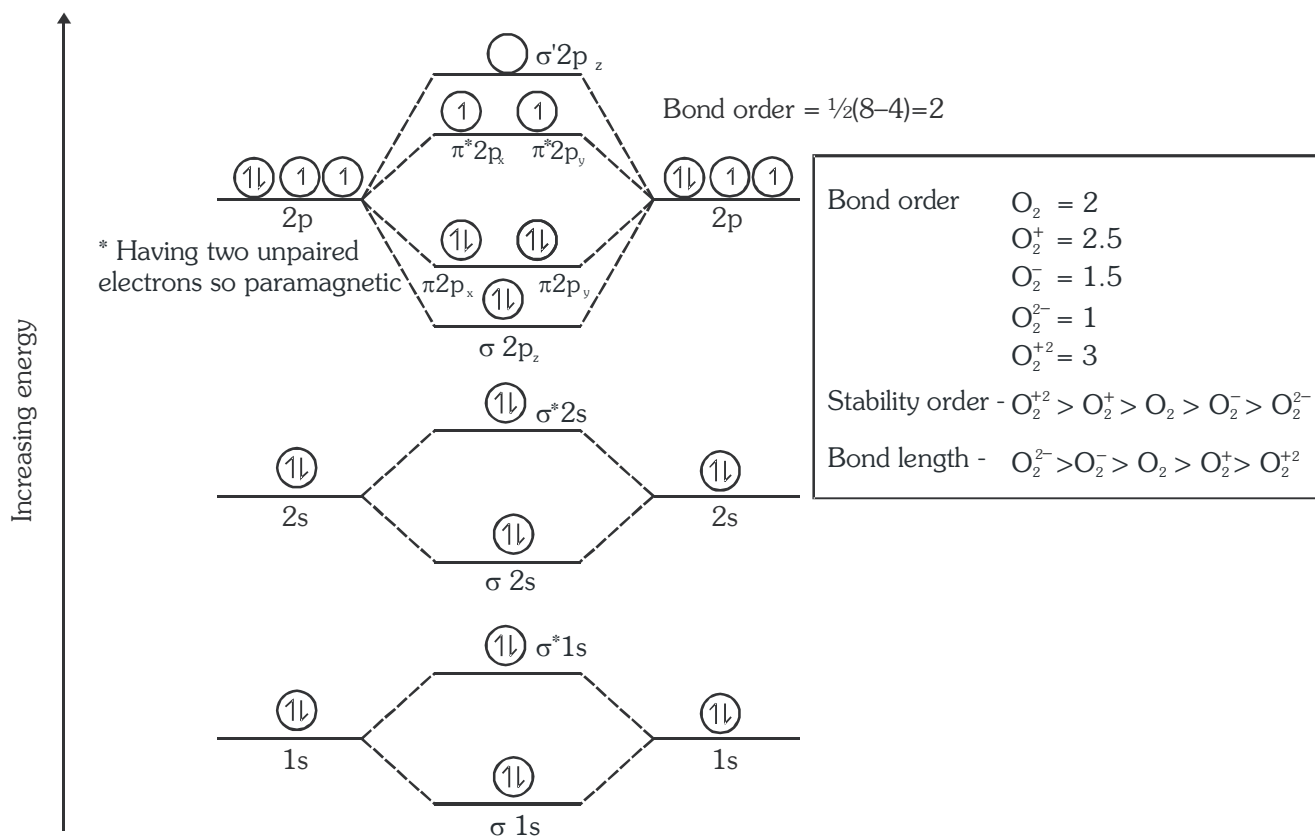
### ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL

#### (A) Energy level diagram for $O_2, F_2, Ne_2$ (Beyond $N_2$ )

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is -

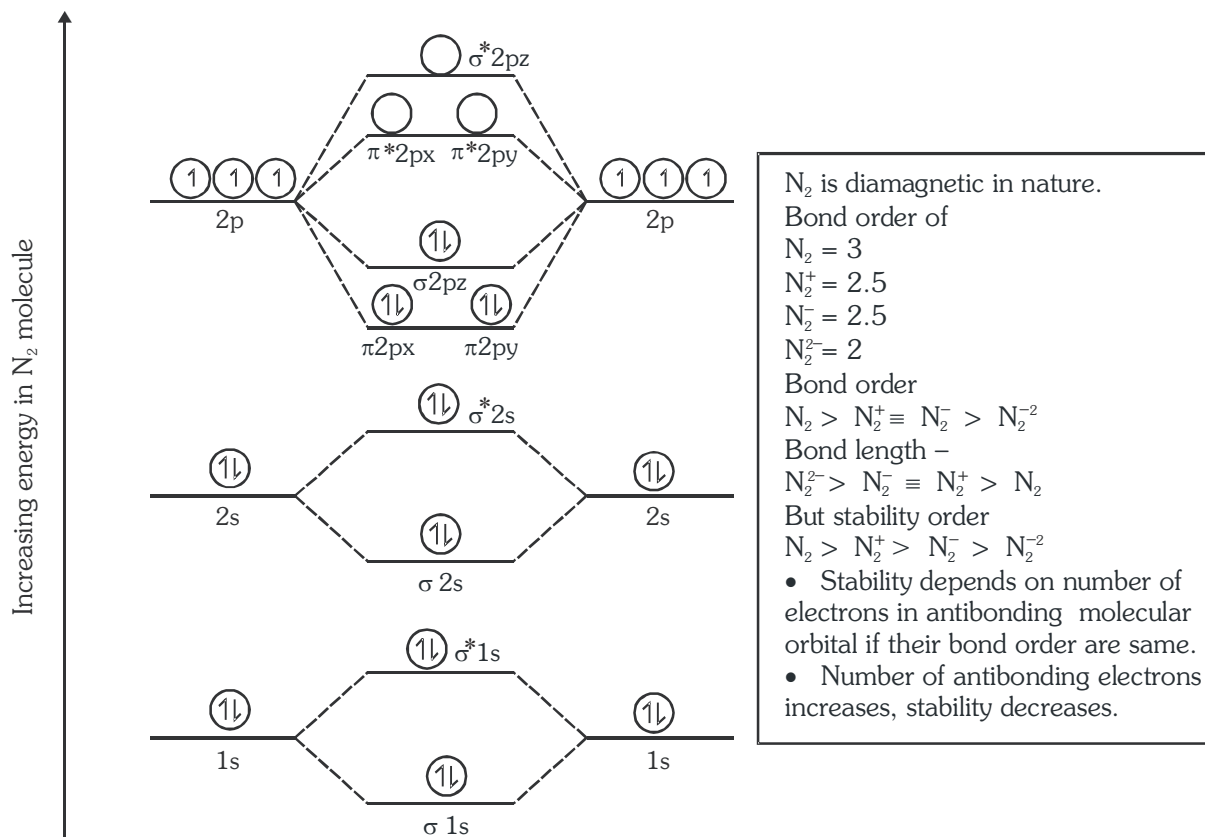
$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x \equiv \pi 2p_y < \pi^* 2p_x \equiv \pi^* 2p_y < \sigma^* 2p_z$

**For  $O_2$  molecule**



**(B) Energy level diagram for B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub> molecules (upto N<sub>2</sub>)**

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x \equiv \pi 2p_y < \sigma 2p_z < \pi^* 2p_x \equiv \pi^* 2p_y < \sigma^* 2p_z$   
**For N<sub>2</sub> molecule**

**Electronic configuration of molecules and their related properties :-**

For writing electronic configuration of diatomic molecules following two rules to be followed-

- Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.
- The pairing in  $\pi 2p_x$  and  $\pi 2p_y$  or  $\pi^* 2p_x$  and  $\pi^* 2p_y$  will take place only when each molecular orbital of identical energy has one electron.

**GOLDEN KEY POINTS**

- Bond order :-**  $\frac{1}{2}[N_b - N_a]$   $N_b$  = Total number of bonding electron  
 $N_a$  = Total number of antibonding electron

**Application of bond order :**

- Bond length :-** (distance between two nuclei)  $\text{Bond length} \propto \frac{1}{\text{Bond order}}$   
 If  $\left. \begin{matrix} N_b > N_a \\ N_b < N_a \\ N_b = N_a \end{matrix} \right\}$   $\left. \begin{matrix} \text{Molecule exists} \\ \text{Molecule do not exists} \end{matrix} \right\}$
- Stability of molecule :-**  $\text{stability} \propto \text{Bond order of molecule}$
- Dissociation energy :-**  $\text{Bond dissociation energy} \propto \text{Bond order}$
- Magnetic property :-**
  - When electron in MO are paired — diamagnetic
  - When electron in MO are unpaired — paramagnetic



## Bonding in molecules

### (a) Hydrogen molecule

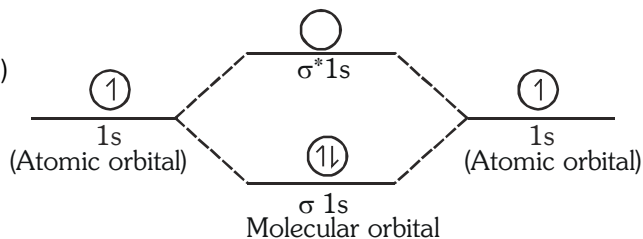
Having two H atoms with one electron each ( $1s^1$ )

M.O. configuration of  $H_2 = (\sigma 1s)^2 (\sigma^* 1s)^0$

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [N_b - N_a] \\ &= \frac{1}{2} [2 - 0] = 1 \text{ ie. single bond.} \end{aligned}$$

Having paired electron so diamagnetic.

Stability  $\rightarrow$  quite stable (having single bond)



### (b) $H_2^+$ ion —

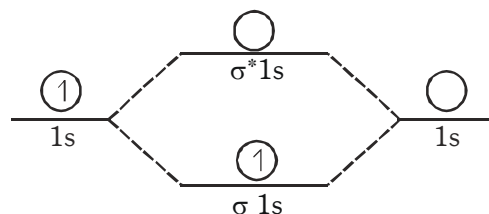
Configuration of  $H_2^+ = (\sigma 1s)^1 (\sigma^* 1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

$$\text{Bond order} = \frac{1}{2} [1 - 0] = \frac{1}{2}$$

Less stable. (In comparison to  $H_2$ )



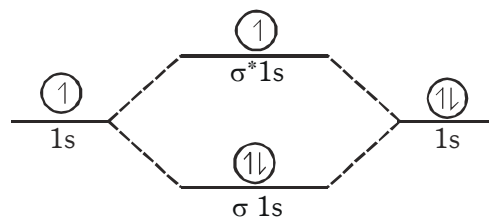
### (c) $H_2^-$ anion -

M.O. configuration -  $(\sigma 1s)^2 (\sigma^* 1s)^1$

Paramagnetic

$$\text{Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$

Stability is less than  $H_2^+$  because  $H_2^-$  contain an ABMO electron



Stability order	$H_2$	$H_2^+$	$H_2^-$
Bond order	1.0	0.5	0.5

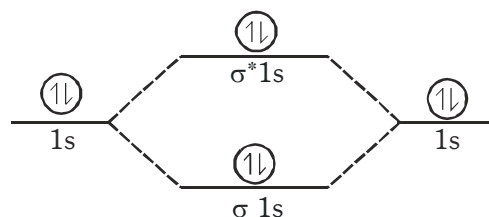
### (d) Helium molecule ( $He_2$ )

M.O. configuration -  $(\sigma 1s)^2 (\sigma^* 1s)^2$

Diamagnetic

$$\text{Bond order} = \frac{1}{2} [2 - 2] = 0 \text{ (zero)}$$

- Bond order zero indicates no linkage between He atoms. Hence  $He_2$  molecule does not exist.



## Comparison between VBT and MOT

1. According to VBT electron moves around only one nucleus	1. According to MOT electron moves under influence of two or more nuclei
2. Orbitals are monocentric	2. Orbitals are polycentric
3. According to VBT $O_2$ is diamagnetic	3. According to MOT $O_2$ is paramagnetic



## BEGINNER'S BOX-6

1. Which of the following is incorrect regarding the MO theory ?
  - (1) The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
  - (2) The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.
  - (3) In a stable molecule, the number of electrons in bonding molecular orbitals is always equal to that in antibonding molecular orbitals.
  - (4) Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.
2. If the z-axis is the molecular axis, then  $\pi$  MOs are formed by the overlap of—
  - (i)  $p_z$  and  $p_z$                       (ii)  $p_y$  and  $p_y$                       (iii)  $s_z$  and  $p_z$                       (iv)  $p_x$  and  $p_x$
  - (1) (ii), (iv)                      (2) (ii), (iii)                      (3) (i), (ii)                      (4) (i), (iii)
3. If the z-axis is taken as the internuclear axis, then which of the following combinations of atomic orbitals is a nonbonding combination ?
  - (1)  $s$  and  $p_y$                       (2)  $p_x$  and  $d_{yz}$                       (3)  $p_x$  and  $p_y$                       (4) all of these
4. Which of the following is the correct order of stability ?
  - (1)  $H_2 > H_2^+ > He_2 > He_2^+$  (2)  $H_2 > He_2^+ > H_2^+ > He_2$  (3)  $H_2 > H_2^+ > He_2^+ > He_2$  (4)  $H_2 > He_2 > He_2^+ > He_2^+$
5. Bond order in  $C_2^+$  is:-
  - (1)  $\frac{1}{2}$                       (2)  $\frac{2}{3}$                       (3)  $\frac{3}{2}$                       (4) 1
6. In which of the following set, the value of bond order will be 2.5:-
  - (1)  $O_2^+$ , NO,  $NO^{+2}$ , CN                      (2) CN,  $NO^{+2}$ ,  $CN^-$ ,  $F_2$
  - (3)  $O_2^+$ ,  $NO^{+2}$ ,  $O_2^{+2}$ ,  $CN^-$                       (4)  $O_2^{-2}$ ,  $O_2^-$ ,  $O_2^+$ ,  $O_2$
7. Of the following species which has the highest bond order and shortest bond length :  
NO,  $NO^+$ ,  $NO^{2+}$ ,  $NO^-$ 
  - (1) NO only
  - (2) Bond order of NO is highest and bond length of  $NO^{2+}$  is shortest
  - (3)  $NO^+$  only
  - (4)  $NO^{2+}$  only
8. The diamagnetic molecule is
  - (1) Super oxide ion                      (2) Oxygen molecule
  - (3) Carbon molecule                      (4) Unipositive ion of nitrogen molecule
9. On the basis of molecular orbital theory which molecules does not exist
  - (1)  $H_2$                       (2)  $He_2$                       (3) HeH                      (4)  $Li_2$
10. Maximum bond energy will be shown by the species
  - (1)  $O_2^+$                       (2)  $O_2$                       (3)  $O_2^-$                       (4)  $O_2^{-2}$

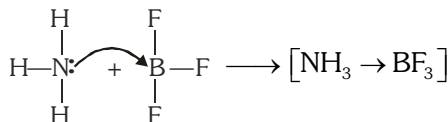


## 2.11 CO-ORDINATE BOND

- (1) It is a covalent bond in which the shared e<sup>-</sup> pair come from one atom is called coordinate bond.
- (2) Necessary conditions for the formation of coordinate bond are -
  - (a) Octet of donor atom should be complete and should have atleast one lone pair of electron.
  - (b) Acceptor atom should have deficiency of at least one pair of electron.

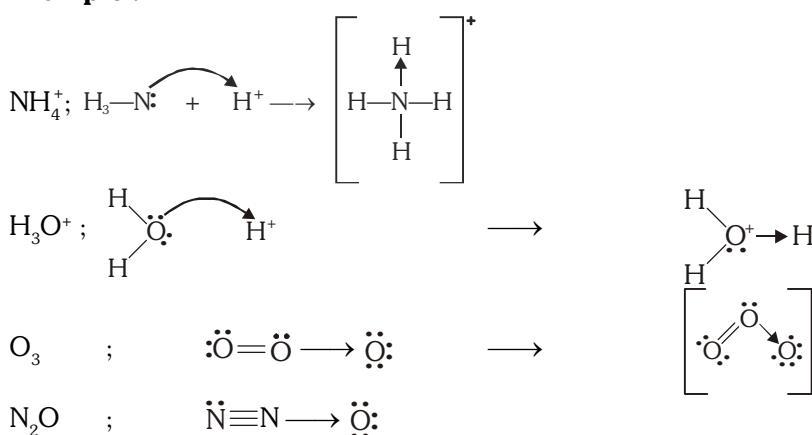


- (3) Atom which provide electron pair for sharing is called donor.
- (4) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.

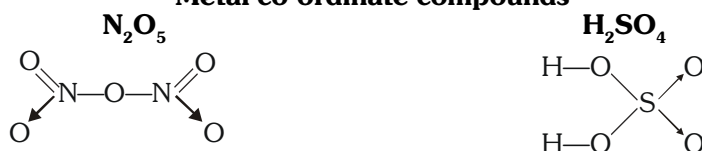


BF<sub>3</sub> is electron deficient compound.

**Example :**



### Metal co-ordinate compounds -



**Compounds** in which Ionic, covalent and co-ordinate bonds are present, are as follows -  
 NH<sub>4</sub>Cl, CuSO<sub>4</sub>, K<sub>4</sub>[Fe(CN)<sub>6</sub>], Na<sub>3</sub>PO<sub>4</sub>, KNO<sub>3</sub>, etc.

## 2.12 FORMAL CHARGE

The difference between the valence electrons in an isolated atom and the number of valence electrons assigned to that atom in a given Lewis structure is called that atom's formal charge. The formal charge, abbreviated FC, on an atom in a Lewis structure is given by the following relationship:

Formal charge on a atom in a Lewis structure

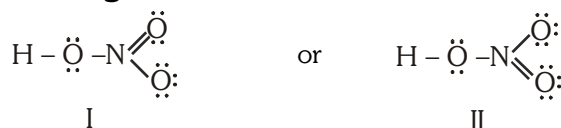
$$= (\text{total number of valence electrons in the isolated atom}) - (\text{Total number of nonbonding electrons}) - \frac{1}{2} (\text{total number of bonding electrons}) \dots (i)$$

$$\text{or} \quad \text{FC} = (\text{Valence electrons}) - (\text{Nonbonding electrons}) - \frac{1}{2} (\text{bonding electrons})$$

$$= (\text{Valence electrons or group number}) - [(\text{Number of unshared } e^-s) + (\text{Number of bonds})]$$

To find the formal charge, we count the bonding electrons as though they are equally shared between the two bonded atoms.

**Q. Calculate the formal charges on the various atoms of nitric acid (HNO<sub>3</sub>) molecule which has been described by the following Lewis structures:**



**The H atom :** It has one valence electron, zero lone pair (or zero nonbonding electrons), and forms one bond (two bonding electrons).

Substituting in Eq. (i), we write  $FC = (1) - (0) - \frac{1}{2}(2) = 0$ .

**The O atom bonded to H:** It has six valence electrons, two lone pairs (or four nonbonding electrons), and from two bonds (or four bonding electrons).

Hence, we write  $FC = (6) - (4) - \frac{1}{2}(4) = 0$ .

**The N atom:** It has five valence electrons, zero lone pair (or zero nonbonding electrons), and forms four bonds (or has eight bonding electrons).

Thus, we write  $FC = (5) - (0) - \frac{1}{2}(8) = +1$

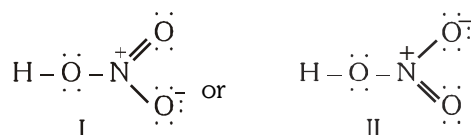
**The end O atom in N = O:** It has six valence electrons in the free state *but* in the Lewis structure (I or II), it has two lone pairs (or four nonbonding electrons) and forms two bonds (or has four bonding electrons).

Thus, we can write  $FC = (6) - (4) - \frac{1}{2}(4) = 0$

**The end O atom in N – O :** It has six valence electrons in the free state but in the Lewis structure (I or II), it has three lone pairs or six nonbonding electrons and forms one bond (or has two bonding electrons).

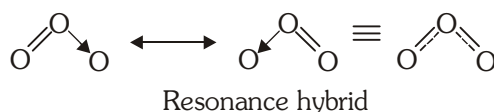
thus, we write  $FC = (6) - (6) - \frac{1}{2}(2) = -1$

We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as



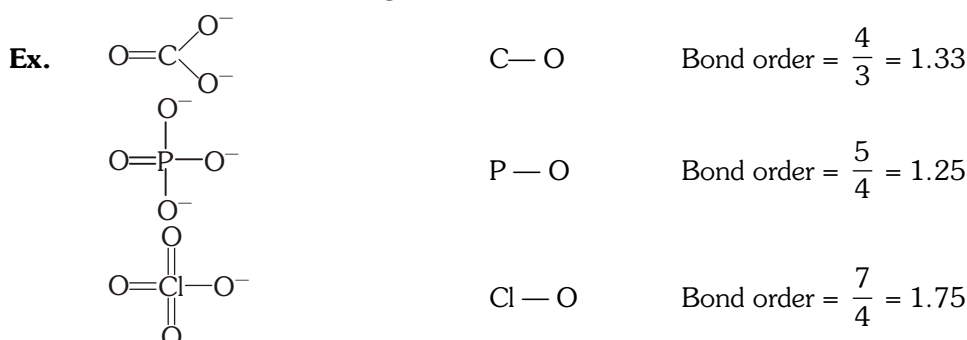
## 2.13 RESONANCE

- It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single Lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O—O = 1.48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



**Note :** To calculate bond order in the polyatomic molecule or ion use following formula :

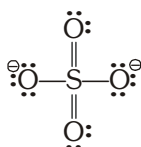
$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$





## BEGINNER'S BOX-7

1. Which of the following ions has resonating structures ?  
 (1)  $\text{SO}_4^{2-}$  (2)  $\text{PO}_4^{3-}$  (3)  $\text{SO}_3^{2-}$  (4) All of these
2. How many resonating structures can be drawn for  $\text{NO}_2$ ?  
 (1) Six (2) Four (3) Five (4) Two
3. Which of the following is true for nitrate anion  
 (1) Formal charge on N is zero (2) Bond order of NO bond is  $\frac{4}{3}$   
 (3) Average formal charge on oxygen is  $-\frac{1}{3}$  (4) There are 2  $\pi$ -bonds in the ion
4. Which of the following contains Co-ordinate and covalent bonds:-  
 (a)  $\text{N}_2\text{H}_5^+$  (b)  $\text{H}_3\text{O}^+$  (c)  $\text{HCl}$  (d)  $\text{H}_2\text{O}$   
 Correct answer is :-  
 (1) a & d (2) a & b (3) c & d (4) Only a
5. The correct statement for the reaction –  
 $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$  :-  
 (1) Hybridisation state is changed (2) Bond angle increases  
 (3)  $\text{NH}_3$  act as a Lewis acid (4) Regular geometry is changed
6. The number of coordinate bonds presents in  $\text{SO}_3$  molecule are  
 (1) 1 (2) 2 (3) 3 (4) 4
7. One of the resonating structure of  $\text{SO}_4^{2-}$  is



Which set of formal charge on oxygen and bond order is correct

- (1) 0.5 and 1.5 (2) 1.5 and 3 (3) 2 and 3 (4) 1.5 and 1.5
8. Resonance is not shown by -  
 (1)  $\text{C}_6\text{H}_6$  (2)  $\text{CO}_2$  (3)  $\text{CO}_3^{2-}$  (4)  $\text{SiO}_2$
9. Bond length of C – O is minimum in –  
 (1)  $\text{CO}$  (2)  $\text{CO}_2$  (3)  $\text{CO}_3^{2-}$  (4)  $\text{HCOO}^-$

### Subjective Type Questions

10. Discuss resonance and formal charge in  $\text{N}_3^-$  and  $\text{N}_2\text{O}$ ?
11. Give the average formal charge and average bond order of XO bond in the following oxy compounds?  
 (a)  $\text{SO}_4^{2-}$  (b)  $\text{SO}_3^{2-}$  (c)  $\text{NO}_2^-$  (d)  $\text{ClO}_2^-$  (e)  $\text{ClO}_3^-$   
 (f)  $\text{ClO}_4^-$  (g)  $\text{HCO}_3^-$  (h)  $\text{CO}_3^{2-}$  (i)  $\text{HSO}_3^-$  (j)  $\text{PO}_4^{3-}$



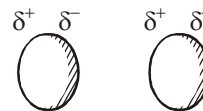
## 2.14 METALLIC BOND

- (1) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (2) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (3) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (4) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (5) Due to small ionisation energy the valence electrons or metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.
- (6) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

## WEAKER FORCES

### 2.15 Vander Waal's Forces

- (a) These are weak; non directional, non valence force of attraction among neutral species.
- (b) These are electrical in nature, due to induced polarity caused by temporary displacement of electrons towards one end of the inert atoms, becoming a temporary dipole.
- (c) This temporary dipole in one molecule can induce opposite dipoles in surrounding molecule due to displacement of electrons, one end becomes -ve and other +ve. These partially charged ends, induce surrounding molecules accordingly.
- (d) Strength of vander waal force depends on ease of distortion of electron cloud.



van der Waal's force  $\propto$  size of atom or molecule  $\propto$  atomic wt. or molecular weight.

- (e) Therefore m.p. and b.p. of noble gas elements (inert gas atom) and halogens increases down the group.

#### Types of van der Waal's Forces

- (a) **Keesom force or dipole dipole force** - one dipole molecule orient the other dipole molecule, to bring opposite ends close to each other for attraction. This is called orientation effect. Example - HCl, H<sub>2</sub>O, NH<sub>3</sub> etc.
- (b) **Debye force or dipole induce dipole force :-** Forces which results from the interaction of a permanent dipole and induced dipole are called Debye force.  
eg. When non-polar substance like benzene come in contact with polar molecules like NH<sub>3</sub>, induced dipole moment in benzene appears (Induction effect).
- (c) **London dispersion force or Instantaneous dipole instantaneous induce dipole attraction :-**

Due to vibration or moment to atom electron cloud and nuclei shifts temporarily towards opposite ends, leads to attraction between them, eg. In atoms of noble gases and halogens.



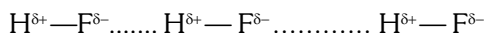
## 2.16 HYDROGEN BONDING

### Definition

- (a) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom.



- (b) It is not formed in ionic compounds.  
 (c) H-bond forms in polar covalent compounds, (not in non-polar).  
 (d) It is very weak bond but stronger than vander waal's force.  
 (e) It is also known as dipole-dipole attraction.



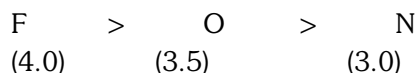
### Main condition for H-bonding

- (a) H— should be covalently bonded with high electro -ve element like F, O, N.  
 (b) Atomic size of electro -ve element should be small.

Order of atomic size is -

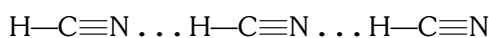


Order of electronegativity is -

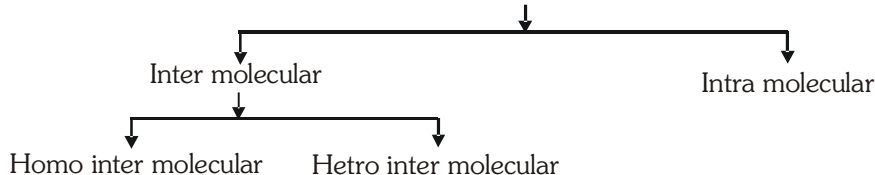


- (c) Strength of H-bond  $\propto$  Electronegativity of Z (element)  $\propto \frac{1}{\text{atomic size of Z}}$

- (d) Hydrogen bonding occurs in HCN, due to ( $-C \equiv N$ ) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.



### TYPES OF HYDROGEN BONDING

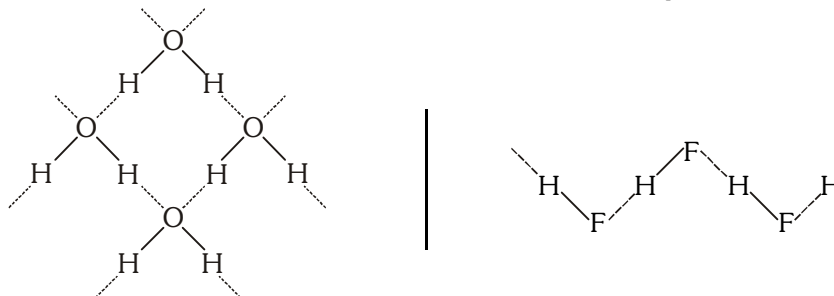


### Intermolecular H-Bond

H-bond formation between two or more molecules of either the same or different compounds known as **Inter molecular H-bonding**.

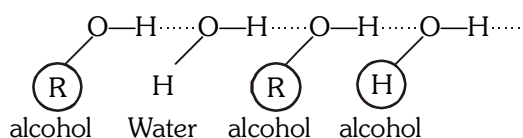
These are of two types :-

- (i) **Homo intermolecular** :- H-bond between molecules of same compound.



- (ii) **Hetro intermolecular** :- H-bond between molecules of different compounds

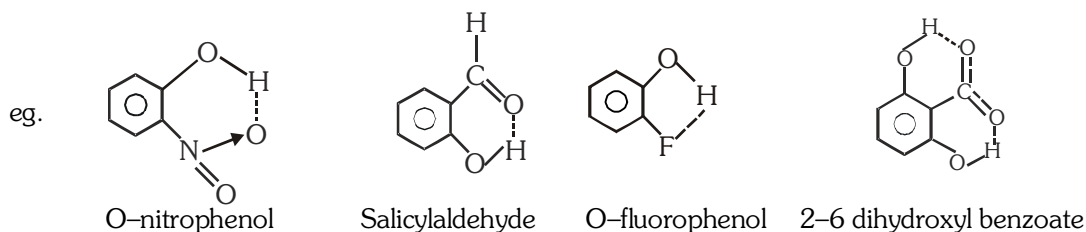
**Eg.** between alcohol and water



## Intramolecular H-bond

It takes place within the molecule.

- (a) H-bonded with electronegative element of a functional group, form H-bond with another electronegative element present on nearest position on the same molecule.
- (b) This type of H-bond is mostly occurred in organic compounds (Aromatic)
- (c) It results in ring formation (Chelation).

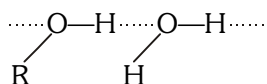


## Effect of H-bond on Physical Properties

### (A) Solubility

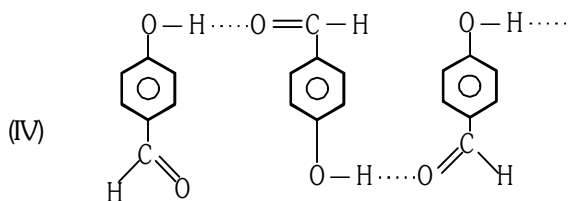
#### (a) Inter molecular H-bonding

- (I) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H-bonding.  
**Ex.** - Alcohol in water



Other examples - Glucose, Fructose etc. dissolve in water.

- (II) Ketone, ether, alkane etc. are insoluble (no H-bond). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H-bonding interrupts.
- (III) Solubility order-  $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH}$

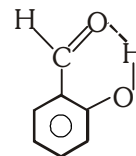


p-hydroxy benzaldehyde.

It can form H-bond with water molecule so it can dissolve.

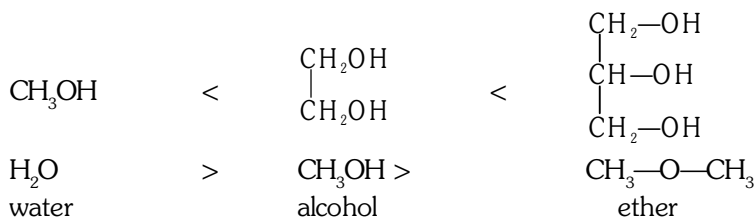
#### (b) Intra molecular H-bonding

- (I) It decreases solubility as it form chelate by H-bonding, so H- is not free for other molecule.
- (II) It can not form H-bond with water molecule so it can not dissolve.



### (B) Viscosity

H-bond associates molecules together so viscosity increases.

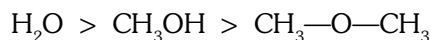


**(C) Surface Tension**

Surface tension of a liquid  $\propto$  extent of H-bonding.

**(D) Melting point and boiling point**

(I) Due to intermolecular H-bond M.P. & B.P. of compounds increases.



(II) Boiling points of VA, VIA, VIIA hydrides are as shown below :



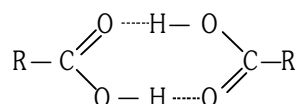
(III) But sudden increase in boiling point of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  is due to H-bonding.

(IV)  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$  (BP comparison due to combined effect of strength and number of H bond)

Intramolecular H-bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal force. So M.P. and B.P. are low.

**(E) Molecular weight**

Molecular wt. of  $\text{CH}_3\text{COOH}$  is double of its molecular formula, due to dimer formation occur by H-bonding.



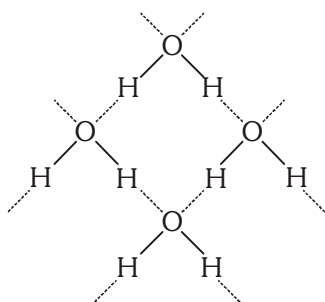
**(F) Physical states**

$\text{H}_2\text{O}$  is liquid while  $\text{H}_2\text{S}$  is gas.

Water and Ice :- Both have H-bonding even then density of ice is less than water.

Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of H-bond.

$\text{H}_2\text{O}$  becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.

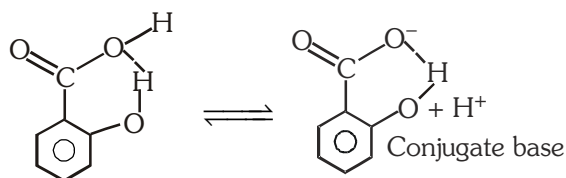


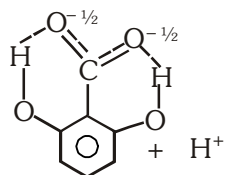
**GOLDEN KEY POINTS**

**Effect of intramolecular H-bonding**

**● Strength of acid**

(I) The formation of intramolecular H-bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid  
2, 6 - dihydroxy benzoic acid > salicylic acid > benzoic acid.





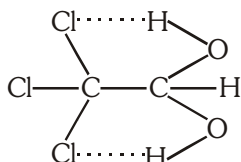
2, 6-dihydroxy benzoate ion.

(II)  $\text{C}_2\text{H}_5\text{SH}$  is more acidic than  $\text{C}_2\text{H}_5\text{OH}$ . In  $\text{C}_2\text{H}_5\text{OH}$ , H-bond forms so  $\text{H}^+$  is not free.

(III)  $\text{HF}$  is weaker acid than  $\text{HI}$ , due to H-bond in  $\text{H}-\text{F}$ ,  $\text{H}^+$  is not free

● **Stability of chloral hydrate**

If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to H-bonding).



Chloral hydrate

## BEGINNER'S BOX-8

- Two ice cubes are pressed over each other until they unite to form one block. The force mainly responsible for holding them together is—
  - (1) van der Waals force
  - (2) dipole-dipole interaction
  - (3) H bonding
  - (4) covalent bonding
- The vapor pressure of *o*-nitrophenol at any given temperature is predicted to be—
  - (1) higher than that of *p*-nitrophenol
  - (2) lower than that of *p*-nitrophenol
  - (3) same as that of *p*-nitrophenol
  - (4) higher or lower depending upon the size of the vessel
- The hydrogen bond is strongest in:—
  - (1)  $\text{O}-\text{H} \cdots \text{S}$
  - (2)  $\text{S}-\text{H} \cdots \text{O}$
  - (3)  $\text{F}-\text{H} \cdots \text{F}$
  - (4)  $\text{O}-\text{H} \cdots \text{O}$
- $\text{H}_2\text{O}$  boils at higher temperature than  $\text{H}_2\text{S}$ , because it is capable of forming:—
  - (1) Ionic bonds
  - (2) Covalent bonds
  - (3) Hydrogen bonds
  - (4) Metallic bonds
- Maximum number of H-bonding is shown by
  - (1)  $\text{H}_2\text{O}$
  - (2)  $\text{H}_2\text{Se}$
  - (3)  $\text{H}_2\text{S}$
  - (4)  $\text{HF}$
- Which is the weakest among the following types of bonds ?
  - (1) Debye force
  - (2) Metallic bond
  - (3) Dipole-dipole bond
  - (4) Hydrogen bond
- The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because :
  - (1)  $\text{NO}_2$  group at *p*-position behaves in a different way from that at *o*-position
  - (2) intramolecular hydrogen bonding exists in *p*-nitrophenol
  - (3) there is intermolecular hydrogen bonding in *p*-nitrophenol
  - (4) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol
- In which molecule the Vander Waals force (dispersion force) is likely to be the most important in determining the m.pt. and b.pt. :
  - (1)  $\text{Br}_2$
  - (2)  $\text{CO}$
  - (3)  $\text{H}_2\text{S}$
  - (4)  $\text{HCl}$
- Covalent-molecules are usually held in a crystal structure by
  - (1) Dipole-dipole attraction
  - (2) Electrostatic attraction
  - (3) Hydrogen bond
  - (4) Van-der waal's attraction
- In solid argon the atoms are held together
  - (1) by ionic bonds
  - (2) by hydrogen bonds
  - (3) By vander-waals forces
  - (4) By hydrophobic bonds



## 2.17 IONIC OR ELECTROVALENT BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.

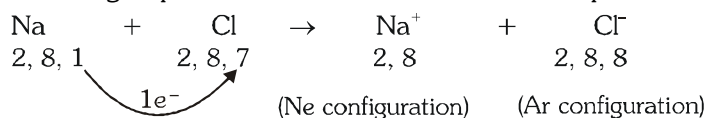
Electro +ve atom loses electron (group IA to IIIA)

Electro -ve atom gains electron (group VA to VIIA)

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Nature of ionic bond  $\propto$  Electronegativity difference.

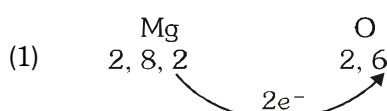
e.g. IA and VIIA group elements form maximum ionic compound.



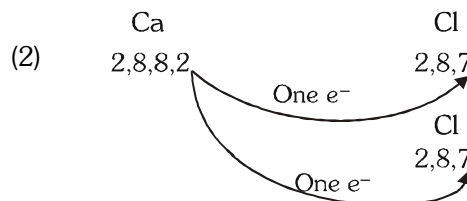
More the distance between two elements in periodic table more will be ionic character of bond.

Total number of electron lose or gained is called electrovalency.

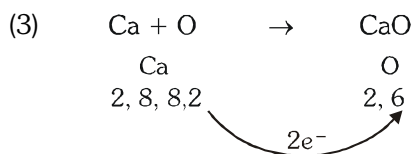
Example –



electrovalency of Mg = 2  
electrovalency of O = 2



electrovalency of Ca = 2  
electrovalency of Cl = 1



electrovalency of Ca = 2  
electrovalency of O = 2

The force of attraction is equal in all direction so ionic bond is non-directional. A definite three dimensional structure is formed called crystal lattice. Energy released during the formation of one mole crystal lattice is called lattice energy.

Ionic compound do not have molecular formula. It has only empirical formula.

e.g. NaCl is empirical formula of sodium chloride

### Conditions for Forming Ionic Bonds

Formation of Ionic bond depends upon these three factors –

#### (a) Ionisation energy :

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)

Lesser Ionisation energy  $\rightarrow$  Greater tendency to form cation.



#### (b) Electron affinity :

Amount of energy released when an electron is added to an isolated gaseous atom to form -ve ion (anion) energy released.

Higher electron affinity  $\rightarrow$  Greater tendency to form anion



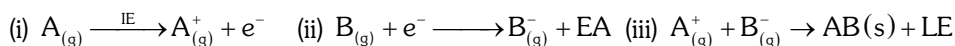
- (c) **Lattice energy** - (Energy released) Amount of energy released when one mole of crystal lattice is formed

Higher lattice energy  $\rightarrow$  Greater will be the stability or strength of ionic compound.  
or Amount of energy required to break the crystal.

- (d) **Overall lowering of energy :**

Energy must be released during bond formation.

Energy changes are involved in the following steps –



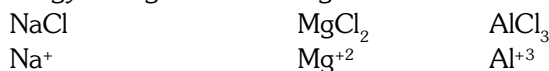
This concludes that for lower value of IE and higher value of EA there is more ease of formation of the ionic compound which is summarised as Born Haber Cycle.

## GOLDEN KEY POINTS

### ● Factors affecting lattice energy

- (1) Magnitude of charge  $\rightarrow U \propto z^+ z^-$  (Ionic charge)

Lattice energy  $\propto$  Magnitude of charge



- $\longrightarrow$
- Lattice energy increases
  - Charge of cation increases


- (2) Size of Cation :- Lattice energy  $\propto \frac{1}{r^+ + r^-}$

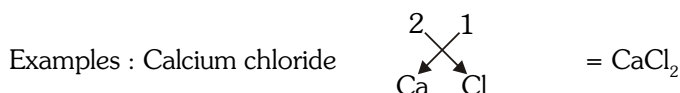


- $\longrightarrow$
- Size of cation increasing
  - Size of anion is constant
  - Lattice energy decreases.

### ● Representation of formula of compounds :

- (1) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as A<sup>+</sup>B<sup>-</sup>
- (2) Write their electrovalencies in figure at the top of each symbol as A<sup>x</sup>B<sup>y</sup>

- (3) Now apply criss cross rule as  , i.e. formula A<sub>y</sub>B<sub>x</sub>.

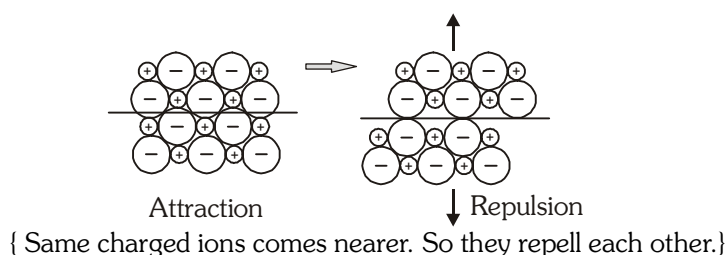


### Properties of Ionic Compound

- (a) **Physical state** –

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness  $\rightarrow$





**(b) Isomorphism –**

- (1) Two compounds are said to be isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.
- (2) They have similar crystal structure.

Example –

	Na <sup>+</sup>	F <sup>-</sup>	Mg <sup>+2</sup>	O <sup>-2</sup>
Valency	+1,	-1	+2,	-2
electronic configuration	2, 8	2, 8	2, 8	2, 8
similarly	Ca <sup>+2</sup>	2Cl <sup>-1</sup>	2K <sup>+1</sup>	S <sup>-2</sup>
	2, 8, 8	2, 8, 8 } 2, 8, 8 }	2, 8, 8 } 2, 8, 8 }	2, 8, 8

**(c) Boiling point and melting point –**

Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

**(d) Conductivity –**

It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity order                      Solid state < fused state < Aqueous solution

**(e) Solubility –**

Highly soluble in Polar solvents like water.

Less soluble in non polar solvents like benzene.

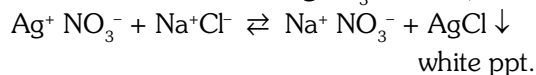
**Ex.** NaCl form a true solution in water but is colloid in benzene

**(f) Ionic reaction –**

(a) Ionic compounds shows ionic reaction and covalent compounds shows - molecular reaction.

(b) Ionic reactions are faster than molecular reaction because of free ions.

e.g. When NaCl is added in AgNO<sub>3</sub> solution, white ppt of AgCl is formed at once.



**(g)** Ionic bond non-directional and does not show stereo isomerism

## 2.18 Polarisation (Fajan's Rule) (Covalent Nature in Ionic Bond)

When a cation approaches an anion closely the positive charge of a cation attract the electron cloud of the anion towards itself, due to the electrostatic force of attraction between them.

At the same time cation also repel the positively charge nucleus of anion.

Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarisation of the anion by the cation and anion is called Polarised.

### Polarisation Power

The ability of cation to polarised a nearby anion is called Polarisation power of cation.



### Polarizability

Ability of an anion to get polarised by the cation.

Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

[Polarisation  $\propto$  Covalent character]

Magnitude of polarisation depends upon a no. of factors, suggested by Fajan and are known as Fajan's rule.

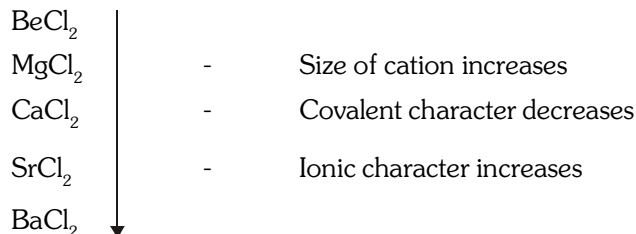


## Fajan's Rule (Factors Affecting Polarisation)

(a) **Size of cation** : Polarisation of the anion increases as the size of cation decreases.

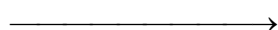
$$\text{Polarisation} \propto \frac{1}{\text{size of cation}}$$

eg. In a group



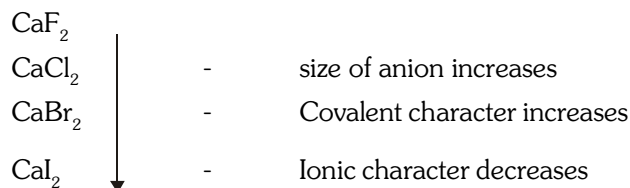
Greatest polarising power of Be<sup>2+</sup>, shows its maximum covalent character

In a period — Na<sup>+</sup>, Mg<sup>+2</sup>, Al<sup>+3</sup>, Si<sup>+4</sup>



- Cation size decreases
- Covalent character increases

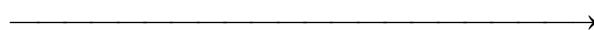
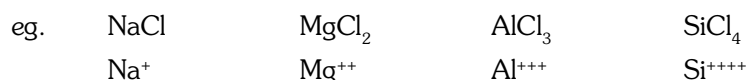
(b) **Size of anion** :- If the size of the anion increases for a given cation, the covalent character increases.  
Polarisation  $\propto$  size of anion.



(c) **Charge on cation and anion** :-

Polarisation  $\propto$  charge on cation or anion

(i) **Polarisation (covalent character)  $\propto$  Charge on cation**



- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)

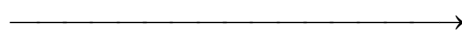
**Ex.** Write the increasing order of M.P. & B.P. of following compounds.



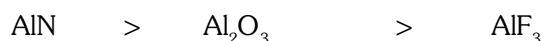
**Ans.** (1) Sn<sup>+4</sup> < Sn<sup>+2</sup>      (2) Fe<sup>+3</sup> < Fe<sup>+2</sup>      (3) Pb<sup>+4</sup> < Pb<sup>+2</sup>

(Charge on cation  $\propto$  polarisation power  $\propto$  covalent character  $\propto \frac{1}{\text{M.P.}}$ )

(ii) **Polarisation  $\propto$  Charge of anion**



- Charge increases
- Covalent character increases



Charge on anion  $\propto$  polarisation  $\propto$  covalent nature  $\propto \frac{1}{\text{M.P.}}$

**(d) Electronic configuration of cation : -**

Order of Polarisation power :  $8e^- < (18+2)e^- < 18e^-$

$\text{CuCl} \longrightarrow \text{Cu}^+ \quad 2, 8, 18 \quad (\text{Covalent})$

$\text{NaCl} \longrightarrow \text{Na}^+ \quad 2, 8 \quad (\text{Ionic})$

$\text{Cu}^+$  and  $\text{Na}^+$  both the cation (Pseudo inert & inert respectively) have same charge and size but polarising power of  $\text{Cu}^+$  is more than  $\text{Na}^+$  because -

$$\begin{array}{ccc} z_{\text{eff}} \text{ of } ns^2p^6 \text{ (inert)} & < & z_{\text{eff}} \text{ of } ns^2p^6d^{10} \text{ (pseudo inert)} \\ \text{Na}^+ & < & \text{Cu}^+ \\ (\text{Ionic}) & & (\text{Covalent}) \end{array}$$

So  $\text{CuCl}$  has more covalent character than  $\text{NaCl}$ .

**Order of covalent character**

- $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$
- $\text{SF}_2 < \text{SF}_4 < \text{SF}_6$
- $\text{CaCl}_2 < \text{FeCl}_2 < \text{FeCl}_3$
- $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2$
- $\text{SrCl}_2 < \text{SnCl}_2 < \text{CdCl}_2$
- $\text{ZnCl}_2 < \text{CdCl}_2 < \text{HgCl}_2$

**Note :**

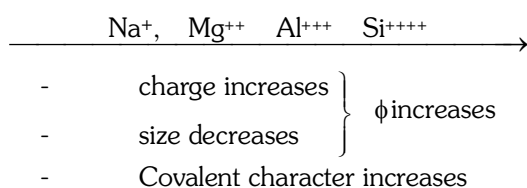
Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi (\text{phi}) = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

**To determine covalent and ionic character of molecule**

$$\phi \propto \frac{\text{Covalent Character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period  $\phi$  increases so covalent character increases.



From top to bottom in a group  $\phi$  decreases so covalent, character decreases.

$\text{Li}^+$	
$\text{Na}^+$	Size increases (charge is fix)
$\text{K}^+$	$\phi$ decreases
$\text{Rb}^+$	Hence covalent character decreases
$\text{Cs}^+$	



**BEGINNER'S BOX-9**

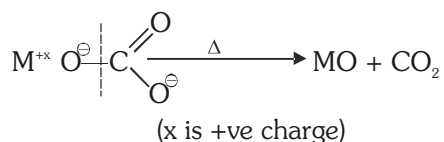
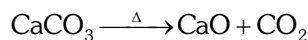
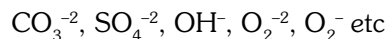
1. The electrovalency of the element is equal to the–  
(1) number of electrons lost  
(2) number of electrons gained  
(3) number of electrons transferred  
(4) number of electrons lost or gained by the atom of the element during the formation of ions of ionic compound
2. Which of the following polar solvents has the highest dielectric constant?  
(1)  $\text{H}_2\text{O}$  (2)  $\text{D}_2\text{O}$  (3)  $\text{CH}_3\text{OH}$  (4)  $\text{C}_2\text{H}_5\text{OH}$
3. Which of the following cations possesses neither noble gas nor pseudo noble gas configurations?  
(i)  $\text{Bi}^{3+}$  (ii)  $\text{Pb}^{2+}$  (iii)  $\text{Sn}^{2+}$  (iv)  $\text{Tl}^+$   
(1) (ii), (iii) (2) (i), (iv) (3) (i), (ii), (iii) (4) (i), (ii), (iii), (iv)
4. Ionic bond formation involves :  
(1) Elimination of protons (2) Sharing of electrons  
(3) Overlapping of orbitals (4) Formation of octets
5. The hydration of ionic compounds involves –  
(1) Evolution of heat (2) Weakening of attractive forces  
(3) Dissociation into ions (4) All
6. The hydration energy of  $\text{Mg}^{+2}$  is greater than the hydration energy of  
(1)  $\text{Al}^{+3}$  (2)  $\text{Mg}^{+3}$  (3)  $\text{Na}^+$  (4)  $\text{Be}^{+2}$
7. Among the following which compounds will show the highest lattice energy ?  
(1)  $\text{KF}$  (2)  $\text{NaF}$  (3)  $\text{CsF}$  (4)  $\text{RbF}$
8. The lattice energy of the lithium is in the following order :  
(1)  $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$  (2)  $\text{LiCl} > \text{LiF} > \text{LiBr} > \text{LiI}$   
(3)  $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$  (4)  $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
9. Among  $\text{LiCl}$ ,  $\text{BeCl}_2$ ,  $\text{BCl}_3$  and  $\text{CCl}_4$ , the covalent bond character follows the order :  
(1)  $\text{LiCl} < \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$  (2)  $\text{LiCl} > \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$   
(3)  $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$  (4)  $\text{LiCl} > \text{BeCl}_2 > \text{BCl}_3 > \text{CCl}_4$



## 2.19 THERMAL DECOMPOSITION

### Thermal stability of metal carbonates

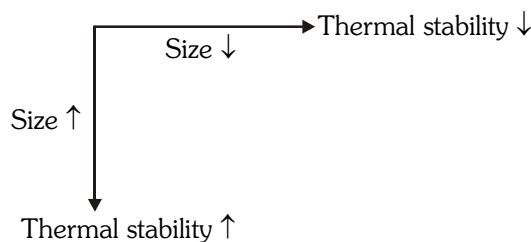
Thermal stability of compound having poly atomic anion



Polarising Power ( $\uparrow$ ) Thermal Stability ( $\downarrow$ )

$$\text{Thermal stability} \propto \frac{1}{\text{Pol.power}} \propto \frac{\text{size of cation}}{\text{charge of cation}}$$

**Compounds having poly atomic anions :**



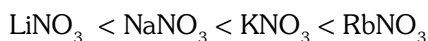
**For fluoride, hydride & normal oxide**

$$\left[ \text{Thermal stability} \propto \frac{1}{\text{size}} \right] \text{ for a group}$$

$$[\text{Thermal stability} \propto \Delta \text{EN}] \text{ for a period}$$

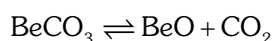
### Thermal Stability order

#### For Example



**Note :**

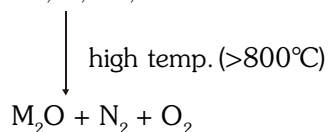
- (i)  $\text{LiHCO}_3$  and IIA group bicarbonate does not exist in solid state.
- (ii) Carbonate, Sulphates & hydroxide of Na, K, Rb & Cs do not decompose at high temperature only melt.
- (iii)  $\text{BeCO}_3$  is kept in  $\text{CO}_2$  atmosphere due to less thermal stability.



## Heating Effect

- (a) Metal carbonate  $\xrightarrow{\Delta}$  metal oxide +  $\text{CO}_2$
- (b) Metal hydroxide  $\xrightarrow{\Delta}$  metal oxide +  $\text{H}_2\text{O}$
- (c) Metal bicarbonate  $\xrightleftharpoons{\Delta}$  metal carbonate +  $\text{CO}_2$  +  $\text{H}_2\text{O}$
- (d) Ammonium salts having  $\text{CO}_3^{-2}$ ,  $\text{PO}_4^{-3}$ ,  $\text{SO}_4^{-2}$ , X-anion (non oxidising or weak oxidising) gives  $\text{NH}_3$  gas on decomposition.  
Ammonium salt having  $\text{Cr}_2\text{O}_7^{-2}$ ,  $\text{ClO}_3^{-1}$ ,  $\text{NO}_2^{-1}$ ,  $\text{NO}_3^{-1}$  (strong oxidising anion) gives  $\text{N}_2$  or  $\text{N}_2\text{O}$  gas on decomposition.
- (e) Metal nitrate  $\xrightarrow{\Delta}$  metal oxide +  $\text{NO}_2$  +  $\text{O}_2$

Except : Na, K, Rb, Cs nitrate  $\xrightarrow{\text{low temp.}}$   $\text{MNO}_2$  +  $\frac{1}{2} \text{O}_2$



### Note :

- (i) Some less stable metal oxide like  $\text{Ag}_2\text{O}$  &  $\text{HgO}$  further decompose into metal & oxygen.
- (ii) Metal salts having high percentage of oxygen like  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  &  $\text{KClO}_3$  give  $\text{O}_2$  gas on decomposition.

## Complete following reactions :

$\text{PbCO}_3 \xrightarrow{\Delta}$	$\text{FeCO}_3 \xrightarrow{\Delta}$
$\text{ZnCO}_3 \xrightarrow{\Delta}$	$\text{MgCO}_3 \cdot \text{CaCO}_3 \xrightarrow{\Delta}$
$\text{CuCO}_3 \cdot \text{Cu(OH)}_2 \xrightarrow{\Delta}$	$\text{NaCO}_3 \cdot 10\text{H}_2\text{O} \longrightarrow \text{X} \longrightarrow \xrightarrow{\Delta}$
$2\text{NaHCO}_3 \xrightarrow{\Delta}$	$\text{NH}_4\text{NO}_2 \xrightarrow{\Delta}$
$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta}$	$(\text{NH}_4)_2\text{SO}_4 \xrightarrow{\Delta}$
$(\text{NH}_4)_2\text{CO}_3 \xrightarrow{\Delta}$	$\text{Ba(N}_3)_2 \text{ or } \text{NaN}_3 \xrightarrow{\Delta}$
$\text{Pb(NO}_3)_2 \xrightarrow{\Delta}$	$\text{Zn(NO}_3)_2 \xrightarrow{\Delta}$
$\text{Ca(NO}_3)_2 \xrightarrow{\Delta}$	$\text{LiNO}_3 \xrightarrow{\Delta}$
$\text{NaNO}_3 \xrightarrow{400^\circ\text{C}}$	$\text{PbCl}_4 \xrightarrow{\Delta}$
$\text{FeCl}_3 \xrightarrow{\Delta}$	$\text{AuCl}_3 \xrightarrow{\Delta}$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{<200^\circ\text{C}} \text{A} \xrightarrow{>200^\circ\text{C}} \text{B} \xrightarrow{800^\circ\text{C}}$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta}$
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{<200^\circ\text{C}} \text{A} \xrightarrow{>200^\circ\text{C}} \text{B} \xrightarrow{800^\circ\text{C}}$	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta}$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{<200^\circ\text{C}} \text{A} \xrightarrow{>200^\circ\text{C}} \text{B} \xrightarrow{750^\circ\text{C}}$	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta}$
$\text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\Delta}$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{<200^\circ\text{C}} \text{A} \xrightarrow{>200^\circ\text{C}} \text{B} \xrightarrow{\Delta}$	$\text{MgCl}_2 \cdot \text{H}_2\text{O} \xrightarrow{\Delta}$
$2\text{KMnO}_4 \xrightarrow{\Delta}$	$\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta}$
$2\text{KClO}_3 \xrightarrow{\Delta}$	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta}$



## 2.20 SOLUBILITY OF IONIC COMPOUNDS

### (a) Solubility of ionic compounds :

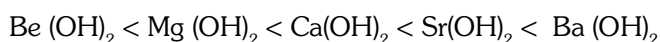
Soluble in polar solvents like water which have high dielectric constant

#### **Factors affecting solubility of ionic compounds :**

- (i) Dielectric constant of the solvent increases the solubility of compound increases
- |                                |       |                  |      |
|--------------------------------|-------|------------------|------|
| HF                             | → 120 | H <sub>2</sub> O | → 81 |
| H <sub>2</sub> SO <sub>4</sub> | → 102 | D <sub>2</sub> O | → 79 |
- (ii) If heat of hydration of ions exceeds the lattice energy (L.E.) of ionic compounds, the ionic compounds will be soluble in water.
- Lattice energy as well as hydration energy depend on the size of ions. Both lattice energy and hydration energy decrease with increase in ionic size.

Two general rule, regarding the solubility is that -

(a) If the anion and the cation are of comparable size, the cationic radius will influence the lattice energy. Since lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.



Solubility increases →

(b) If the anion is large compared to the cation, (i.e. compound contain ions with widely different radii) the lattice energy will remain almost constant i.e. change is very small within a particular group. Since the hydration energies decrease down a group, solubility will decrease.



Solubility decreases →

#### **Note :**

- If common ion is small like Na<sup>+</sup>, Li<sup>+</sup>, O<sup>2-</sup>, F<sup>-</sup>, OH<sup>-</sup>, IIA cation then lattice energy dominates.
- If common ion is large like Cs<sup>+</sup>, Rb<sup>+</sup>, Br<sup>-</sup>, I<sup>-</sup>, polyatomic anion like CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> then hydration energy dominates.

### **Some important solubility orders:**

#### **Examples**

- BeSO<sub>4</sub> > MgSO<sub>4</sub> > CaSO<sub>4</sub> > SrSO<sub>4</sub> > BaSO<sub>4</sub> (SO<sub>4</sub><sup>2-</sup> larger)
- CsF > CsCl > CsBr > CsI [Cs<sup>+</sup> (larger)]
- BeS > MgS > CaS > SrS > BaS (S<sup>2-</sup> larger)

### **Important facts about solubility**

- (i) All metal chlorides are soluble except Ag, Pb, Hg
- (ii) All metal sulphides are insoluble except : IA and ammonium
- (iii) Highly insoluble sulphides are of Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Bi<sup>3+</sup>
- (iv) All hydroxides are insoluble except IA, lower IIA (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) and ammonium
- (v) Most insoluble hydroxides are of Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>
- (vi) All metal nitrate, Acetate, perchlorate are soluble in water
- (vii) Generally metal sulphates are soluble in water except Ag, Hg, Pb, Ca, Sr, Ba
- (viii) All alkali metal salts are soluble in water except . LiF, Li<sub>2</sub>CO<sub>3</sub>, Li<sub>3</sub>PO<sub>4</sub>, Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>



## 2.21 MELTING POINT

Melting point of ionic compounds

The two factors which mainly influence the melting point of ionic compound are

- (i) Lattice enthalpy                      (ii) Polarisation



Melting point of ionic compound > covalent compound

Except                      Giant molecules  
   ↓  
                                 Diamond, Carborundum (SiC)  
                                 Norbide (B<sub>4</sub>C), Silica (SiO<sub>2</sub>) Borazone (BN)<sub>x</sub>

Order of Hardness : Diamond > Norbide > SiC > Al<sub>2</sub>O<sub>3</sub>

### Some important melting point orders :

#### Examples



### Melting Point and Boiling Point of non-metallic molecules

- (i) CH<sub>3</sub>—O—CH<sub>3</sub> < C<sub>2</sub>H<sub>5</sub>OH (boiling point)
- (ii) CH<sub>4</sub> < SiH<sub>4</sub> < GeH<sub>4</sub> < SnH<sub>4</sub> < PbH<sub>4</sub> (boiling point)
- (iii) I-Cl > Br<sub>2</sub> (boiling point)
- (iv) H<sub>2</sub> < O<sub>2</sub> < H<sub>2</sub>O (boiling point)
- (v) CH<sub>3</sub>-OH < H<sub>2</sub>O (surface tension)
- (vi) HCl < HNO<sub>3</sub> < H<sub>2</sub>SO<sub>4</sub> < H<sub>3</sub>PO<sub>4</sub> (melting point)
- (vii) H<sub>2</sub>O < D<sub>2</sub>O (boiling point)
- (viii) O-nitro phenol < p-nitro phenol (boiling point)
- (ix) H<sub>2</sub>O >> H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te (melting point)
- (x) NH<sub>3</sub> >> PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> (melting point)
- (xi) HCl < HBr < HI < HF (boiling point)
- (xii) HCl < HBr < HF < HI (melting point)





## Melting point & boiling point of elements

- (i)  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$  (melting point)
- (ii)  $\text{Be} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$  (melting point)
- (iii) **3d series**  
Melting point  $\propto$  number of unpaired electrons  
 $\therefore$  In 3d series (MP) maximum = Cr (chromium)  
In 4d series (MP) maximum = Mo  
In 5d series (MP) maximum = W
- (iv)  $3d < 4d < 5d$  (melting point)
- (v)  $\text{Zn} > \text{Cd} > \text{Hg}$  (Melting point)  
 $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$  (boiling point)  
 $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$  (boiling point)  
 $\text{N}_2 < \text{P}_4 < \text{As}_4$  (boiling point)  
 $\text{O}_2 < \text{S}_8 < \text{Se}_8 < \text{Te}_8$  (boiling point)  
 $\text{H}_2 > \text{He}$  (melting point)

**Note :** Maximum melting point in Boron family  $\rightarrow$  Boron

Minimum melting point in Boron family  $\rightarrow$  Gallium

Maximum melting point in all elements  $\rightarrow$  Carbon

Minimum melting point in all elements  $\rightarrow$  Helium

Maximum melting point in Metals  $\rightarrow$  Tungsten

Minimum melting point in Metals  $\rightarrow$  Mercury

## COLOUR OF COMPOUNDS

More the covalent character, more will be the colour intensity.

Colour intensity  $\propto \phi$  (Covalent character)

**Example :**

$\text{AgF}$ (Colourless)	$\text{AgCl}$ (White)	$\text{AgBr}$ (Light yellow)	$\text{AgI}$ (Dark yellow)
------------------------------	--------------------------	---------------------------------	-------------------------------

 $\rightarrow$

### BEGINNER'S BOX-10

**Arrange in order of thermal stability :**

1.  $\text{BeCO}_3, \text{MgCO}_3, \text{CaCO}_3, \text{SrCO}_3, \text{BaCO}_3$   
 $\text{KO}_2, \text{RbO}_2, \text{CsO}_2$   
 $\text{NH}_3, \text{PH}_3, \text{AsH}_3, \text{SbH}_3, \text{BiH}_3$   
 $\text{H}_2\text{O}, \text{H}_2\text{S}, \text{H}_2\text{Se}, \text{H}_2\text{Te}$   
 $\text{BeO}, \text{MgO}, \text{CaO}, \text{SrO}, \text{BaO}$   
 $\text{NH}_3, \text{H}_2\text{O}, \text{HF}$   
 $\text{NaF}, \text{MgF}_2, \text{AlF}_3$   
 $\text{Na}_2\text{SO}_4, \text{MgSO}_4, \text{Al}_2(\text{SO}_4)_3$   
 $\text{CCl}_4, \text{SiCl}_4, \text{GeCl}_4, \text{SnCl}_4, \text{PbCl}_4$



## 2. Give solubility order for :-

- |                                     |                              |
|-------------------------------------|------------------------------|
| (i) alkali metal hydroxide          | (ii) Sodium halides          |
| (iii) alkali metal per chlorates    | (iv) alkali metal oxides     |
| (v) alkaline earth metal carbonates | (vi) alkali metal carbonates |
| (vii) alkali metal bicarbonates     | (viii) silver halides        |
| (ix) lead (II) halides              | (x) mercury (II) halides     |

## 3. Give the order of melting points

- |  |   |   |
|--|---|---|
| • $\text{Na}_2\text{O}$ , $\text{MgO}$ , $\text{Al}_2\text{O}_3$ | • $\text{CaCl}_2$ , $\text{FeCl}_2$ , $\text{FeCl}_3$ | • $\text{NaF}$ , $\text{MgO}$ , $\text{ScN}$ , $\text{TiC}$ |
| • $\text{SnCl}_2$ , $\text{SnCl}_4$                              | • $\text{KCl}$ , $\text{CuCl}$ , $\text{CuCl}_2$      |   |

# ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4						
	Ans.	3	4	2	1						

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8		
	Ans.	3	1	4	3	1	3	1	2		

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10	11
	Ans.	3	1	3	2	2	2	3	4	4	3	4

BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	3	2	3	3	2	1	2	1	3

BEGINNER'S BOX-5	Que.	1	2	3	4	5					
	Ans.	1	2	3	1	2					

BEGINNER'S BOX-6	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	4	3	3	1	3	3	2	1

BEGINNER'S BOX-7	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	4	4	2	2	2	2	1	4	1	

BEGINNER'S BOX-8	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	3	1	1	3	1	4	3

BEGINNER'S BOX-9	Que.	1	2	3	4	5	6	7	8	9		
	Ans.	4	1	4	4	4	3	2	1	3		



## EXERCISE-I (Conceptual Questions)

### OCTET RULE :

- Among the following element group number is not equals to valence electrons -  
(1) Na (2) N  
(3) Ne (4) None
- Which of the following does not act as lewis acid ?  
(1)  $\text{BF}_3$  (2)  $\text{SnCl}_4$   
(3)  $\text{CCl}_4$  (4)  $\text{SF}_4$

### COVALENT BOND

- The strength of bonds by 2s - 2s, 2p - 2p and 2p - 2s overlapping has the order :-  
(1)  $s - s > p - p > s - p$   
(2)  $s - s > p - s > p - p$   
(3)  $p - p > s - p > s - s$   
(4)  $p - p > s - s > p - s$
- In which of the excitation state of chlorine  $\text{ClF}_3$  is formed:-  
(1) In ground state  
(2) In third excitation state  
(3) In first excitation state  
(4) In second excitation state
- A sigma bond is formed by the overlapping of :-  
(1) s-s orbital alone  
(2) s and p orbitals alone  
(3) s-s, s-p or p-p orbitals along internuclear axis  
(4) p-p orbital along the sides
- Which overlapping is involved in HCl molecule :-  
(1) s-s overlap (2) p-p overlap  
(3) s-d overlap (4) s-p overlap
- Which is not characteristic of  $\pi$ -bond:-  
(1)  $\pi$  - bond is formed when a sigma bond already formed  
(2)  $\pi$  - bond are formed from hybrid orbitals  
(3)  $\pi$  - bond may be formed by the overlapping of p-orbitals  
(4)  $\pi$ -bond results from lateral overlap of atomic orbitals  
  
 $\pi$  bond is formed :-  
(1) By overlapping of hybridised orbitals  
(2) Overlapping of s - s orbitals  
(3) Head on overlapping of p -p orbitals  
(4) By p - p collateral overlapping  
  
Which of the following overlapping is strongest ?  
(1) 1s - 1s (2) 2p - 2p  
(3) 2s - 2p (4) 1s - 2p
- p-p overlapping will be observed in the molecules of:  
(1) Hydrogen (2) Hydrogen bromide  
(3) Hydrogen chloride (4) Chlorine

- Which compound of xenon is not possible  
(1)  $\text{XeF}_2$  (2)  $\text{XeF}_4$  (3)  $\text{XeF}_5$  (4)  $\text{XeF}_6$
- Similarity of fluorine and oxygen may not be attributed to-  
(1) Their atomic and ionic radii are closely similar  
(2) The atom of both elements attain an octet of electrons in their valence shell  
(3) Both of them are highly electronegative elements  
(4) Both form stable  $p\pi - p\pi$  multiple bonds with themselves
- Higher is the bond order, greater is -  
(1) Bond dissociation energy  
(2) Covalent character  
(3) Bond length  
(4) Paramagnetism

### HYBRIDISATION

- In the protonation of  $\text{H}_2\text{O}$ , change occurs in  
(1) Hybridisation state of oxygen  
(2) Shape of molecule  
(3) Hybridisation and shape both  
(4) None
- In the compound  
 $\overset{1}{\text{CH}_2}=\overset{2}{\text{CH}}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_2}-\overset{5}{\text{C}}\equiv\overset{6}{\text{CH}}$ , the  $\text{C}^2 - \text{C}^3$  bond is formed by the overlapping of :-  
(1)  $sp - sp^2$  (2)  $sp^3 - sp^3$   
(3)  $sp - sp^3$  (4)  $sp^2 - sp^3$
- Among the following species identify the isostructural pairs:-  
 $\text{NF}_3$ ,  $\text{NO}_3^-$ ,  $\text{BF}_3$ ,  $\text{H}_3\text{O}^+$ ,  $\text{HN}_3$   
(1)  $[\text{NF}_3, \text{NO}_3^-]$  and  $[\text{BF}_3, \text{H}_3\text{O}^+]$   
(2)  $[\text{NF}_3, \text{HN}_3]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
(3)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
(4)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{HN}_3, \text{BF}_3]$
- Which of the set of species have same hybridisation state but different shapes:-  
(1)  $\text{NO}_2^+$ ,  $\text{NO}_2$ ,  $\text{NO}_2^-$   
(2)  $\text{ClO}_4^-$ ,  $\text{SF}_4$ ,  $\text{XeF}_4$   
(3)  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{OF}_2$   
(4)  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{ClO}_4^-$



- 18.** Which of the following elements can not exhibit  $sp^3d$  hybridisation state:-  
 (a) C (b) P (c) Cl (d) B  
 Correct answer is:-  
 (1) a, c (2) a, d (3) b, c (4) b, d
- 19.** Which of the following species are expected to be planar:-  
 (a)  $NH_3$  (b)  $NH_3^{2+}$  (c)  $CH_3^+$  (d)  $PCl_3$   
 The correct answer is:-  
 (1) b and c (2) c and d  
 (3) b and d (4) a and d
- 20.** In which following set of compound/ion has linear shape  
 (1)  $CH_4$ ,  $NH_4^+$ ,  $BH_4^-$  (2)  $CO_3^{2-}$ ,  $NO_3^-$ ,  $BF_3$   
 (3)  $NO_2^+$ ,  $CO_2$ ,  $XeF_2$  (4)  $BeCl_2$ ,  $BCl_3$ ,  $CH_4$
- 21.** Which order of decreasing bond angle is correct:-  
 (1)  $CCl_4 > BF_3 > NO_2^+$   
 (2)  $NH_3 > NCl_3 > NBr_3$   
 (3)  $Br_2O > Cl_2O > OF_2$   
 (4)  $PCl_3 > PBr_3 > PI_3$
- 22.** Which of the following set is not correct:-  
 (1)  $SO_3$ ,  $O_3$ ,  $NH_4^+$  all have coordinate bonds  
 (2)  $H_2O$ ,  $NO_2$ ,  $ClO_2^-$ , all are 'V' shape molecules  
 (3)  $I_3^-$ ,  $ICl_2^-$ ,  $NO_2^+$ ; all are linear molecules  
 (4)  $SF_4$ ,  $SiF_4$ ,  $XeF_4$  are tetrahedral in shape
- 23.** Shape of a molecule having 4 bond pairs and two lone pairs of electrons, will be :-  
 (1) Square planar (2) Tetrahedral  
 (3) Linear (4) Octahedral
- 24.** The shape of  $IF_4^+$  will be :-  
 (1) Square planar  
 (2) Tetrahedral  
 (3) Pentagonal bipyramidal  
 (4) Distorted tetrahedral
- 25.** Which of the following has pyramidal shape ?  
 (1)  $BF_3$  (2)  $H_3O^+$   
 (3)  $NO_3^-$  (4)  $CO_3^{2-}$
- 26.** A  $\sigma$  bonded molecule  $MX_3$  is T-shaped. The number of non-bonding pairs of electrons is  
 (1) 0  
 (2) 2  
 (3) 1  
 (4) Can be predicted if atomic number of M is known.
- 27.** Amongst  $CO_3^{2-}$ ,  $AsO_3^{3-}$ ,  $XeO_3$ ,  $ClO_3^-$ ,  $BO_3^{3-}$  and  $SO_3^{2-}$  the non-planar species are :-  
 (1)  $XeO_3$ ,  $ClO_3^-$ ,  $SO_3^{2-}$ ,  $AsO_3^{3-}$   
 (2)  $AsO_3^{3-}$ ,  $XeO_3$ ,  $CO_3^{2-}$   
 (3)  $BO_3^{3-}$ ,  $CO_3^{2-}$ ,  $SO_3^{2-}$   
 (4)  $AsO_3^{3-}$ ,  $BO_3^{3-}$ ,  $CO_3^{2-}$
- 28.** The type of hybrid orbitals used by chlorine atom in  $ClO^-$ ,  $ClO_2^-$ ,  $ClO_3^-$  and  $ClO_4^-$  is/are :-  
 (1)  $sp$ ,  $sp^2$ ,  $sp^3$  and  $sp^3d$  (2)  $sp$  and  $sp^3$   
 (3) Only  $sp^3$  (4) only  $sp$
- 29.** On the basis of hybridization of one s & one p orbitals they are arranged at :-  
 (1) Two orbitals mutually at  $90^\circ$  angle  
 (2) two orbitals mutually at  $180^\circ$  angle  
 (3) Two orbitals mutually at  $120^\circ$  angle  
 (4) Two orbitals mutually at  $150^\circ$  angle
- 30.** Which of the following having a square planar structure is  
 (1)  $NH_4^+$  (2)  $BF_4^-$  (3)  $XeF_4$  (4)  $CCl_4$
- 31.** When p-character of hybridised orbital (formed by s and p orbitals) increases. Then the bond angle  
 (1) Decreases (2) Increases  
 (3) Becomes twice (4) Remains unaltered
- 32.** Which orbitals overlap to form bond in  $OF_2$   
 (1)  $sp^3 - 2p$  (2)  $sp^2 - 2p$   
 (3)  $sp - 2p$  (4)  $p - p$
- 33.** In compounds X, all the bond angles are exactly  $109^\circ 28'$ . X is :  
 (1) Chloromethane  
 (2) Carbon tetrachloride  
 (3) Iodoform  
 (4) Chloroform
- 34.** Among the following orbitals/bonds, the angle is minimum between :  
 (1)  $sp^3$  bonds  
 (2)  $p_x$  and  $p_y$  orbitals  
 (3)  $H-O-H$  bond in water  
 (4)  $sp$  bonds
- 35.** The structure and hybridization of  $Si(CH_3)_4$  is :  
 (1) bent,  $sp$   
 (2) trigonal,  $sp^2$   
 (3) octahedral,  $sp^3d$   
 (4) tetrahedral,  $sp^3$
- 36.** The  $AsF_5$  molecule is trigonal bipyramidal. The hybrid orbitals used by the As atoms for bonding are:  
 (1)  $d_{x^2-y^2}$ ,  $d_{z^2}$ ,  $s$ ,  $p_x$ ,  $p_y$  (2)  $d_{xy}$ ,  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$   
 (3)  $s$ ,  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{z^2}$  (4)  $d_{x^2-y^2}$ ,  $s$ ,  $p_x$ ,  $p_y$



37. When the hybridization state of carbon atom changes from  $sp^3$ ,  $sp^2$  and  $sp$ , the angle between the hybridized orbitals.  
 (1) decrease considerably  
 (2) increase progressively  
 (3) decrease gradually  
 (4) all of these
38. The hybridization states of the central atoms of the ions  $I_3^-$ ,  $ICl_4^-$  and  $ICl_2^-$  are respectively :  
 (1)  $sp^2$ ,  $dsp^2$ ,  $sp^3$   
 (2)  $sp^3d$ ,  $sp^3d^2$  and  $sp^3d$   
 (3)  $sp^3d$ ,  $sp^3d$ ,  $dsp^2$   
 (4)  $sp$ ,  $sp$ ,  $dsp^2$
39. Molecular shapes of  $SF_4$ ,  $CF_4$  and  $XeF_4$  are :-  
 (1) The same, with 2, 0 and 1 lone pairs of electrons respectively  
 (2) The same, with 1, 1 and 1 lone pairs of electrons respectively  
 (3) Different, with 0, 1 and 2 lone pairs of electrons respectively  
 (4) Different, with 1, 0 and 2 lone pairs of electrons respectively
40. Which of the following two are isostructural :-  
 (1)  $XeF_2$ ,  $IF_2^-$  (2)  $NH_3$ ,  $BF_3$   
 (3)  $CO_3^{2-}$ ,  $SO_3^{2-}$  (4)  $PCl_5$ ,  $ICl_5$
41. Select the correct matching :  

List I		List II	
A : $XeF_4$		1. Pyramidal	
B : $XeF_6$		2. T-shape	
C : $XeO_3$		3. Distorted octahedral	
D : $XeOF_2$		4. Square planar	
A	B	C	D
(1) 4	3	1	2
(2) 1	2	3	4
(3) 2	1	3	4
(4) 4	1	3	2
42. Which one of the following pair is a correct with respect to molecular formula of xenon compound and hybridization state of xenon in it :  
 (1)  $XeF_4$ ,  $sp^3$  (2)  $XeF_2$ ,  $sp$   
 (3)  $XeF_2$ ,  $sp^3d$  (4)  $XeF_4$ ,  $sp^2$
43. The xenon compound(s) that are iso-structural with  $IBr_2^-$  and  $BrO_3^-$  respectively are :  
 (1) Linear  $XeF_2$  and pyramidal  $XeO_3$   
 (2) Bent  $XeF_2$  and pyramidal  $XeO_3$   
 (3) Bent  $XeF_2$  and planar  $XeO_3$   
 (4) Linear  $XeF_2$  and tetrahedral  $XeO_3$

## DIPOLE MOMENT

44. Which statement is correct:-  
 (1) All the compounds having polar bonds, have dipole moment  
 (2)  $SO_2$  is non-polar  
 (3)  $H_2O$  molecule is non polar, having polar bonds  
 (4)  $PH_3$  is polar molecule having non polar bonds
45.  $BeF_2$  has zero dipole moment where as  $H_2O$  has a dipole moment because :-  
 (1) Water is linear  
 (2)  $H_2O$  is bent  
 (3) F is more electronegative than O  
 (4) Hydrogen bonding is present in  $H_2O$
46. Which of the following species are symmetrical :-  
 (a)  $XeF_4$  (b)  $XeF_6$   
 (c)  $SO_2$  (d)  $NH_3^{+2}$   
 Correct answer is:-  
 (1) a and b (2) b and c  
 (3) c and d (4) a and d
47. Which of the following molecule have zero dipole moment:-  
 (1)  $BF_3$  (2)  $CH_2Cl_2$   
 (3)  $NF_3$  (4)  $SO_2$
48. The dipole moment of  $NH_3$  is:-  
 (1) Less than dipole moment of  $NCl_3$   
 (2) Higher than dipole moment of  $NCl_3$   
 (3) Equal to the dipole moment of  $NCl_3$   
 (4) None of these
49. Which of the following order of polarities of molecules is correct:-  
 (1)  $HF > NH_3 > PH_3$   
 (2)  $CH_4 > NH_3 > H_2O$   
 (3)  $CH_3Cl < CH_2Cl_2 < CHCl_3$   
 (4)  $BF_3 > BeF_2 > F_2$
50. Which set of molecules is polar :-  
 (1)  $XeF_4$ ,  $IF_7$ ,  $SO_3$  (2)  $PCl_5$ ,  $C_6H_6$ ,  $SF_6$   
 (3)  $SnCl_2$ ,  $SO_2$ ,  $NO_2$  (4)  $CO_2$ ,  $CS_2$ ,  $C_2H_6$
51. Which of the following has symmetrical structure :  
 (1)  $PCl_3$  (2)  $CH_2Cl_2$   
 (3)  $CHCl_3$  (4)  $CCl_4$
52. Species having zero dipole moment :-  
 (1)  $XeF_4$   
 (2) 1,2,4 trichloro benzene  
 (3)  $SF_4$   
 (4)  $CH_2Cl_2$



53. What conclusion can be drawn from the fact that  $\text{BF}_3$  has no dipole moment but  $\text{PF}_3$  does  
 (1)  $\text{BF}_3$  is not symmetrical but  $\text{PF}_3$  is  
 (2)  $\text{BF}_3$  molecule must be linear  
 (3) Atomic radius of P is larger than that of B  
 (4)  $\text{BF}_3$  molecule must be planar triangular
54.  $\text{PCl}_5$  is non polar because :-  
 (1) P – Cl bond is non-polar  
 (2) Its dipole moment is zero  
 (3) P – Cl bond is polar  
 (4) P & Cl have equal electronegativity
55. Dipole moment of  $\text{CO}_2$  is zero which implies that :  
 (1) Carbon and oxygen have equal electronegativities  
 (2) Carbon has no polar bond  
 (3)  $\text{CO}_2$  is a linear molecule  
 (4) Carbon has bond moments of zero value
56. The correct order of dipole moment is :  
 (1)  $\text{CH}_4 < \text{NF}_3 < \text{NH}_3 < \text{H}_2\text{O}$   
 (2)  $\text{NF}_3 < \text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O}$   
 (3)  $\text{NH}_3 < \text{NF}_3 < \text{CH}_4 < \text{H}_2\text{O}$   
 (4)  $\text{H}_2\text{O} < \text{NH}_3 < \text{NF}_3 < \text{CH}_4$
57. Which of the following molecule does not possess a permanent dipole moment :  
 (1)  $\text{H}_2\text{S}$  (2)  $\text{SO}_2$  (3)  $\text{SO}_3^{2-}$  (4)  $\text{CS}_2$
58. Which of the following has the highest value of dipole moment :  
 (1) HCl (2) HF (3) HI (4) HBr

### MOLECULAR ORBITAL THEORY

59. The ion that is isoelectronic with CO and having same bond order is :-  
 (1)  $\text{CN}^-$  (2)  $\text{O}_2^+$  (3)  $\text{O}_2^-$  (4)  $\text{N}_2^+$
60. Which of the following is paramagnetic:-  
 (1)  $\text{O}_2^-$  (2)  $\text{CN}^-$  (3) CO (4)  $\text{NO}^+$
61. In the following which of the two are paramagnetic  
 (a)  $\text{N}_2$  (b) CO (c)  $\text{B}_2$  (d)  $\text{NO}_2$   
 Correct answer is :-  
 (1) a and c (2) b and c  
 (3) c and d (4) b and d
62. The bond order of CO molecule on the basis of molecular orbital theory is  
 (1) Zero (2) 2 (3) 3 (4) 1
63. The energy of  $\sigma_{2s}$  orbital is greater, than  $\sigma_{1s}^*$  orbital because  
 (1)  $\sigma_{2s}$  orbital is bigger than  $\sigma_{1s}^*$  orbital  
 (2)  $\sigma_{2s}$  orbital is a bonding orbital where as  $\sigma_{1s}^*$  is an antibonding orbital  
 (3)  $\sigma_{2s}$  orbital has a greater value of n than  $\sigma_{1s}^*$  orbital  
 (4) None
64. The no. of antibonding electron pair in  $\text{O}_2^-$  is  
 (1) 4 (2) 3  
 (3) 8 (4) 10
65. Which of the following species will have the minimum bond energy  
 (1)  $\text{N}_2$  (2)  $\text{N}_2^-$   
 (3)  $\text{N}_2^+$  (4)  $\text{N}_2^{2-}$
66. Which of the following ion has not bond order of 2.5 ?  
 (1)  $\text{O}_2^-$  (2)  $\text{O}_2^+$   
 (3)  $\text{N}_2^+$  (4)  $\text{N}_2^-$
67. In a homonuclear molecule which of the following set of orbitals are degenerate ?  
 (1)  $\sigma_{2s}$  and  $\sigma_{1s}$  (2)  $\pi_{2p_x}$  and  $\pi_{2p_y}$   
 (3)  $\pi_{2p_x}$  and  $\sigma_{2p_z}$  (4)  $\sigma_{2p_z}$  and  $\pi_{2p_x}^*$

### COORDINATE BOND

68. In Co-ordinate bond, the acceptor atoms must essentially contain in its valency shell an orbital:-  
 (1) With paired electron  
 (2) With single electron  
 (3) With no electron  
 (4) With three electron
69. The bonds present in  $\text{N}_2\text{O}_5$  are :-  
 (1) Only ionic  
 (2) Covalent & coordinate  
 (3) Only covalent  
 (4) Covalent & ionic
70. Dative bond is present in  
 (1)  $\text{SO}_3$  (2)  $\text{NH}_3$   
 (3)  $\text{K}_2\text{CO}_3$  (4)  $\text{BF}_3$
71. Which of the following has no coordinate bond ?  
 (1)  $\text{PH}_3$  (2)  $\text{P}_2\text{H}_6^{+2}$   
 (3)  $\text{P}_2\text{H}_5^+$  (4)  $\text{PH}_4^+$
72. The compound containing co-ordinate bond is :  
 (1)  $\text{H}_2\text{SO}_4$  (2)  $\text{O}_3$   
 (3)  $\text{SO}_3$  (4) All of these

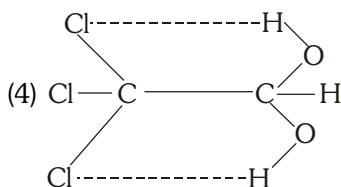
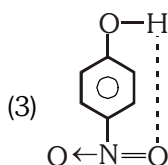
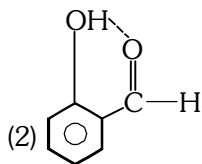
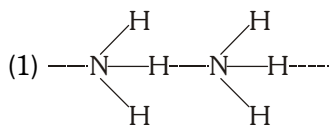
### WEAK FORCES

73. In dry ice the bond present between two molecules is  
 (1) Ionic bond (2) Covalent bond  
 (3) Hydrogen bond (4) Vander Waal
74. Intermolecular hydrogen bonds are not present in:-  
 (1)  $\text{CH}_3\text{CH}_2\text{OH}$  (2)  $\text{CH}_3\text{COOH}$   
 (3)  $\text{C}_2\text{H}_5\text{NH}_2$  (4)  $\text{CH}_3\text{OCH}_3$





75. In which of the following molecule, the shown hydrogen bond is not possible:-



76. Correct order of volatility is:-

- (1)  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
- (2)  $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$
- (3)  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- (4)  $\text{HBr} < \text{HCl} < \text{HI} < \text{HF}$

77. The correct order of volatility is:-

- (1)  $\text{NH}_3 < \text{H}_2\text{O}$
- (2) p-nitro phenol < o-nitro phenol
- (3)  $\text{CH}_3\text{OH} > \text{CH}_3 - \text{O} - \text{CH}_3$
- (4)  $\text{HF} > \text{HCl}$

78. The incorrect order of decreasing boiling points is

- (1)  $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
- (2)  $\text{H}_2\text{O} > \text{H}_2\text{Se} > \text{H}_2\text{S}$
- (3)  $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$
- (4)  $\text{CH}_4 > \text{GeH}_4 > \text{SiH}_4$

79. Acetic acid exists as dimer in benzene due to:-

- (1) Condensation reaction
- (2) Hydrogen bonding
- (3) Presence of carboxyl group
- (4) None of the above

80. Maximum no. of hydrogen bonds formed by a water molecule in ice is

- (1) 4
- (2) 3
- (3) 2
- (4) 1

81. Strongest hydrogen bond is shown by :

- (1) Water
- (2) Ammonia
- (3) Hydrogen fluoride
- (4) Hydrogen sulphide

82. Density of ice is less than that of water because of

- (1) presence hydrogen bonding
- (2) crystal modification of ice
- (3) open porous structure of ice due to hydrogen bonding
- (4) different physical states of these

83.  $\text{NH}_3$  has abnormally high boiling point because it has :

- (1) Alkaline nature
- (2) Distorted shape
- (3)  $\text{sp}^3$  - Hybridisation
- (4) Hydrogen bonding

84. Which of the following is soluble in water ?

- (1)  $\text{CS}_2$
- (2)  $\text{C}_2\text{H}_5\text{OH}$
- (3)  $\text{CCl}_4$
- (4)  $\text{CHCl}_3$

85. KF combines with HF to form  $\text{KHF}_2$ . The compound contains the species :

- (1)  $\text{K}^+$ ,  $\text{F}^-$  and  $\text{H}^+$
- (2)  $\text{K}^+$ ,  $\text{F}^-$  and HF
- (3)  $\text{K}^+$  and  $[\text{HF}_2]^-$
- (4)  $[\text{KHF}]^+$  and  $\text{F}_2$

86. Which of the following compounds show intramolecular hydrogen bonding :

- (A) o-nitrophenol
- (B) p-nitrophenol
- (C) phenol
- (D) salicylaldehyde

- (1) A & B
- (2) A & C
- (3) A & D
- (4) B & C

87. The pair of molecules forming strongest hydrogen bonds are :

- (1)  $\text{SiH}_4$  and  $\text{SiF}_4$
- (2)  $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_3$  and  $\text{CHCl}_3$

- (3)  $\text{H} - \text{C}(=\text{O}) - \text{OH}$  and  $\text{CH}_3 - \text{C}(=\text{O}) - \text{OH}$

- (4)  $\text{H}_2\text{O}$  and  $\text{H}_2$

## IONIC BOND

88. Which one is the correct statement with reference to solubility of  $\text{MgSO}_4$  in water:

- (1) Hydration energy of  $\text{MgSO}_4$  is higher in comparison to its lattice energy
- (2) Ionic potential of  $\text{Mg}^{2+}$  is very low
- (3)  $\text{SO}_4^{2-}$  ion mainly contributes towards hydration energy
- (4) Size of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are similar



- 89.** Conditions for ionic bond formation is/are :  
 (a) Small cation, large anion  
 (b) Low IP of cation, high electron affinity of anion  
 (c) Large cation, small anion and less charge  
 (d) Less lattice energy  
 Correct answer is:  
 (1) a, d (2) b, c and d  
 (3) b and c (4) a, b
- 90.** Capacity of solvent to neutralise charge on ionic compound is called:-  
 (1) Solvation energy (2) Dielectric constant  
 (3) Dipole moment (4) Solubility
- 91.** The force responsible for dissolution of ionic compound in water is –  
 (1) Dipole – dipole forces  
 (2) Ion – dipole force  
 (3) Ion – ion force  
 (4) Hydrogen bond
- 92.** Born Haber cycle is mainly used to determine  
 (1) Lattice energy (2) Electron affinity  
 (3) Ionisation energy (4) Electronegativity
- 93.** An ionic compound  $A^+ B^-$  is most likely to be formed when –  
 (1) Ionization energy of A is low  
 (2) Electron affinity of B is high  
 (3) Electron affinity of B is low  
 (4) Both (1) and (2)
- 94.** The pair of elements which on combination are most likely to form an ionic compound is  
 (1) Na and Ca (2) K and O  
 (3) O and Cl (4) Al and I
- 95.** Choose the compound of each of the following pairs that has the more solubility in water :-  
 (a)  $BeSO_4$ ,  $BaSO_4$  (b)  $NaCl$ ,  $MgCl_2$   
 (c)  $AgCl$ ,  $AgI$   
 (1)  $BeSO_4$ ,  $MgCl_2$ ,  $AgI$  (2)  $BeSO_4$ ,  $NaCl$ ,  $AgCl$   
 (3)  $BaSO_4$ ,  $NaCl$ ,  $AgCl$  (4)  $BaSO_4$ ,  $MgCl_2$ ,  $AgI$
- 96.** Highest melting point would be of  
 (1)  $AlCl_3$  (2)  $LiCl$   
 (3)  $NaCl$  (4)  $BeCl_2$
- 97.** Which of the following substance will have highest b.p.t. ?  
 (1) He (2)  $CsF$   
 (3)  $NH_3$  (4)  $CHCl_3$
- 98.** As compared to covalent compounds electrovalent compounds generally possess  
 (1) High m.p. and high b.p.  
 (2) Low m.p. and low b.p.  
 (3) Low m.p. and high b.p.  
 (4) high m.p. and low b.p.
- 99.** The electronic configuration of metal M is  $1s^2 2s^2 2p^6 3s^1$ . The formula of its oxide will be :  
 (1)  $MO$  (2)  $M_2O$   
 (3)  $M_2O_3$  (4)  $MO_2$
- 100.** Which of the following pairs will form the most stable ionic bond ?  
 (1) Na and Cl (2) Mg and F  
 (3) Li and F (4) Na and F
- 101.** For two ionic solids,  $CaO$  and  $KI$ . Identify the wrong statement among the following :  
 (1) Lattice energy of  $CaO$  is much larger than that of  $KI$   
 (2)  $KI$  is soluble in benzene  
 (3)  $CaO$  has higher melting point  
 (4)  $KI$  has lower melting point
- 102.** Which of the following does not show electrical conduction ?  
 (1) diamond  
 (2) graphite  
 (3) sodium chloride (fused)  
 (4) potassium
- 103.** The most covalent halide is:-  
 (1)  $AlF_3$  (2)  $AlCl_3$   
 (3)  $AlBr_3$  (4)  $AlI_3$
- 104.** Ionic potential ( $\phi$ ) of electropositive element will be highest in which of the following compound:-  
 (1)  $CsCl$  (2)  $MgCl_2$   
 (3)  $AlF_3$  (4)  $SF_6$
- 105.**  $LiCl$  is soluble in organic solvent while  $NaCl$  is not because :-  
 (1) Lattice energy of  $NaCl$  is less than that of  $LiCl$   
 (2) Ionisation potential of Li is more than that of Na  
 (3)  $Li^+$  has more hydration energy than  $Na^+$  ion  
 (4)  $LiCl$  is more covalent compound than that  $NaCl$
- 106.** The most stable carbonate is  
 (1)  $Li_2CO_3$  (2)  $BeCO_3$   
 (3)  $CaCO_3$  (4)  $BaCO_3$
- 107.** Correct order of covalent character of alkaline earth metal chloride in  
 (1)  $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$   
 (2)  $BeCl_2 < CaCl_2 < SrCl_2 < MgCl_2$   
 (3)  $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2$   
 (4)  $SrCl_2 > BeCl_2 > CaCl_2 > MgCl_2$
- 108.** Which of the compound is least soluble in water  
 (1)  $AgF$  (2)  $AgCl$   
 (3)  $AgBr$  (4)  $AgI$





**109.**  $\text{CCl}_4$  is more covalent than  $\text{LiCl}$  because :

- (1) There is more polarization of Cl in  $\text{CCl}_4$
- (2) There is more polarization of Cl in  $\text{LiCl}$
- (3)  $\text{CCl}_4$  has more weight
- (4) None of above

**110.** The M.P. of  $\text{SnCl}_4$  is less than that of  $\text{SnCl}_2$ , the suitable reason for the observed fact is

- (1) There is more charge on  $\text{Sn}^{+4}$
- (2) The size of  $\text{Sn}^{+4}$  is small
- (3) Ionic potential of  $\text{Sn}^{+4}$  is high
- (4) The shape of  $\text{SnCl}_4$  is tetrahedral

**111.** The correct order of decreasing polarisable ions is:

- (1)  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{F}^-$
- (2)  $\text{F}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$
- (3)  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$
- (4)  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$

**112.** Ionic conductances of hydrated  $\text{M}^+$  ions are in the order –

- (1)  $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) > \text{Cs}^+(\text{aq})$
- (2)  $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$
- (3)  $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq}) > \text{K}^+(\text{aq}) > \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$
- (4)  $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$

**113.** Which of the following halides has the highest melting point –

- (1)  $\text{NaCl}$
- (2)  $\text{KCl}$
- (3)  $\text{NaBr}$
- (4)  $\text{NaF}$

**114.** Which of the following does not give an oxide on heating –

- (1)  $\text{MgCO}_3$
- (2)  $\text{Li}_2\text{CO}_3$
- (3)  $\text{ZnCO}_3$
- (4)  $\text{K}_2\text{CO}_3$

**115.** Which decomposes on heating –

- (1)  $\text{NaOH}$
- (2)  $\text{KOH}$
- (3)  $\text{LiOH}$
- (4)  $\text{RbOH}$

**116.** Which of the following forms metal oxide on heating

- (1)  $\text{Na}_2\text{CO}_3$
- (2)  $\text{Li}_2\text{CO}_3$
- (3)  $\text{K}_2\text{SO}_4$
- (4)  $\text{NaHCO}_3$

**117.** Increasing order of stability of –

- I.  $\text{K}_2\text{CO}_3$     II.  $\text{MgCO}_3$     III.  $\text{Na}_2\text{CO}_3$
- (1)  $\text{I} < \text{II} < \text{III}$
  - (2)  $\text{II} < \text{III} < \text{I}$
  - (3)  $\text{II} < \text{I} < \text{III}$
  - (4)  $\text{I} < \text{III} < \text{II}$

**118.** Which of the following carbonate will not decompose on heating :-

- (1)  $\text{BaCO}_3$
- (2)  $\text{ZnCO}_3$
- (3)  $\text{Na}_2\text{CO}_3$
- (4)  $\text{Li}_2\text{CO}_3$

**119.** The decomposition temperature is maximum for:-

- (1)  $\text{BeCO}_3$
- (2)  $\text{CaCO}_3$
- (3)  $\text{K}_2\text{CO}_3$
- (4)  $\text{Li}_2\text{CO}_3$

## EXERCISE-I (Conceptual Questions)

## ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	3	3	3	4	2	4	1	4	3	4	1	2	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	2	1	3	3	4	1	4	2	2	1	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	1	2	2	4	3	2	2	4	1	1	3	1	4	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	1	2	1	3	4	1	4	2	3	1	4	2	1	1
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	3	3	3	2	4	1	2	3	2	1	1	4	4	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	2	4	2	1	3	3	4	2	3	3	3	1	3	2
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	2	1	4	2	2	3	2	1	2	2	2	1	4	4	4
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	
Ans.	4	3	4	1	3	4	4	4	4	3	2	2	3	3	



- 95.** Which pair not shows same shape :-  
 (1)  $I_3^{-1}$ ,  $BeCl_2$  (2)  $BF_3$ ,  $ClO_3^{-1}$   
 (3)  $SO_2$ ,  $H_2O$  (4)  $XeF_4$ ,  $BrF_4^{-}$
- 96.** In which at least one  $\sigma$ -bond of np ( $\sigma_{np}$ ) orbital is present :-  
 (1)  $B_2$  (2)  $O_2$   
 (3)  $C_2$  (4)  $Li_2$
- 97.** Which is correct for dipole moment :-  
 (1)  $NH_3 < NF_3$  (2)  $SO_2 < SO_3$   
 (3)  $NF_3 > BF_3$  (4)  $SO_2 > H_2O$
- 98.** Which of the following is a molecular solid :-  
 (1) solid  $SO_2$  (2) SiC  
 (3) C. (graphite) (4) ZnS
- 99.** The geometry and No. of lone pair on  $ClF_2^{-}$  and  $ClF_4^{-}$  are respectively :-  
 (1) Square planar, 2 & Linear, 3  
 (2) Square Planar, 3 & Linear, 2  
 (3) Linear, 3 & Square planar, 2  
 (4) Tetrahedral, 2 & linear, 3
- 100.** Wrong statement for  $N_3^{-}$  is :-  
 (1) Isoelectronic with  $CO_2$   
 (2) Structure is linear  
 (3) Both N-N bond lengths are unequal in hydrogen azide  
 (4) Oxidation state for Nitrogen is same as in  $NH_2OH$
- 101.** Bond order of which of following pair is different:-  
 (1)  $F_2^{-}$  &  $O_2^{-2}$  (2)  $N_2^{-}$  &  $O_2^{+}$   
 (3)  $C_2$  &  $B_2^{-2}$  (4)  $N_2$  &  $O_2^{2+}$
- 102.** Correct order for Bond angle is  
 (1)  $SO_2 > NH_3$  (2)  $NH_3 < H_2O$   
 (3)  $SO_2 < H_2O$  (4)  $H_2S > NH_3$
- 103.** Which of the following two species have same shape but different hybridisation  
 (1)  $XeF_2$  and  $ICl_2^{-}$  (2)  $NO_2^{+}$  and  $SO_2$   
 (3)  $BeCl_2$  and  $NO_2^{+}$  (4)  $SO_2$  and  $NH_2^{-}$
- 104.** Which of the following has maximum %s character in N-H bond ?  
 (1)  $N_2H_2$  (2)  $NH_4^{+}$  (3)  $NH_3$  (4)  $N_2H_4$

## EXERCISE-II (Previous Year Questions)

## ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	4	2	3	2	1	3	3	1	2	2	2	4	1	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	4	1	3	3	3	4	2	2	1	1	3	1	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	1	2	2	3	4	3	2	3	3	4	3	3	1	1	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	2	3	3	3	1	4	2	1	3	2	4	2	2	1	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	2	2	1	1	2	1	1	4	2,3	1	2	2	2	2
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	2	3	3	1	2	3	2	3	3	3	4	1	4	2
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	
Ans.	3	2	4	4	2	2	3	1	3	4	1	1	4	1	



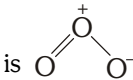

## Directions for Assertion &amp; Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.


- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.  
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.  
 (C) If Assertion is True but the Reason is False.  
 (D) If both Assertion & Reason are false.

- Assertion** : Ionic bonds are formed between metal and nonmetals  
**Reason** : In ionic bonds electrons are shared  
 (1) A (2) B (3) C (4) D
- Assertion** :  $D_2O$  is better solvent for ionic compounds, than  $H_2O$ .  
**Reason** : dielectric constant of  $D_2O$  is higher than  $H_2O$ .  
 (1) A (2) B (3) C (4) D
- Assertion** : Hydrated ionic radius of  $Li^+$  is maximum in IA group elements.  
**Reason** : Lithium is a metal  
 (1) A (2) B (3) C (4) D
- Assertion** :  $LiCl$  exhibits covalent character.  
**Reason** : Lithium is lightest metal.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $K_2CO_3$  do not gives  $CO_2$  gas on heating.  
**Reason** : Value of  $\sqrt{\phi}$  for  $K^+$  is high.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $CO_2$  molecule is non-polar while  $SO_2$  is polar.  
**Reason** : Carbon atom is smaller than sulphur.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $CH_3OH$  is soluble in water  
**Reason** :  $CH_3OH$  is ionic in nature  
 (1) A (2) B (3) C (4) D
- Assertion** : Boiling point of  $H_2O$  is greater than  $C_2H_5OH$ .  
**Reason** : Molecular wt. of  $H_2O$  is higher than  $C_2H_5OH$ .  
 (1) A (2) B (3) C (4) D
- Assertion** :  $NO^+$  is more stable than  $NO^-$ .  
**Reason** :  $NO^+$  do not have electron in antibonding orbitals.  
 (1) A (2) B (3) C (4) D
- Assertion** : In  $MgO$  electrovalency of  $Mg$  is 2.  
**Reason** :  $Mg$  shares two electrons with oxygen.  
 (1) A (2) B (3) C (4) D
- Assertion** : Ionic reactions are faster than molecular reactions.  
**Reason** : Ionic bonds are weaker than covalent bonds.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $LiI$  is more soluble in water than  $LiF$ .  
**Reason** :  $LiI$  has more ionic character.  
 (1) A (2) B (3) C (4) D
- Assertion** : Bond energy of  $H-H$  bond is greater than  $Cl-Cl$  bond.  
**Reason** :  $H_2$  is more covalent than  $Cl_2$ .  
 (1) A (2) B (3) C (4) D
- Assertion** : Ionic compounds tend to be non-volatile.  
**Reason** : Inter ionic forces in these compounds are strong.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $NCl_3$  has pyramidal shape  
**Reason** : In  $NCl_3$  central atom is  $sp^3$  hybridised.  
 (1) A (2) B (3) C (4) D
- Assertion** :  $BF_3$  is planar while  $NF_3$  is non-planar molecule.  
**Reason** :  $B-F$  bond is more polar than  $N-F$  bond.  
 (1) A (2) B (3) C (4) D
- Assertion** : Density of ice is greater than water  
**Reason** : In ice  $H_2O$  molecules are closely packed.  
 (1) A (2) B (3) C (4) D
- Assertion** : Bond order of  $O_2$  and  $BN$  is same.  
**Reason** :  $O_2$  and  $BN$  are isoelectronic  
 (1) A (2) B (3) C (4) D



19. **Assertion** : p-nitrophenol is more viscous than o-nitrophenol.  
**Reason** : In p-nitrophenol, intermolecular H-bonding occurs.  
 (1) A (2) B (3) C (4) D
20. **Assertion** :  $\text{H}_2\text{O}_2$  is not used as solvent for ionic compounds  
**Reason** : Dielectric constant of  $\text{H}_2\text{O}_2$  is low  
 (1) A (2) B (3) C (4) D
21. **Assertion** : Ionic compounds exhibits electrical conductivity in solution state.  
**Reason** : In solution state electrons of ionic compounds are free.  
 (1) A (2) B (3) C (4) D
22. **Assertion** : p-nitrophenol is more volatile than o-nitrophenol.  
**Reason** : Molecular wt. of p-nitrophenol is higher than o-nitrophenol.  
 (1) A (2) B (3) C (4) D
23. **Assertion** :  $\text{N}_2^+$  is more stable than  $\text{N}_2^-$   
**Reason** :  $\text{N}_2^+$  has less electrons in antibonding orbitals.  
 (1) A (2) B (3) C (4) D
24. **Assertion** :  $\text{SO}_4^{2-}$  is square planar in shape  
**Reason** :  $\text{SO}_4^{2-}$  has  $\text{sp}^3\text{d}$  hybridisation  
 (1) A (2) B (3) C (4) D
25. **Assertion** :  $\text{NF}_3$  molecule is more polar than  $\text{NH}_3$  molecule.  
**Reason** :  $\text{NF}_3$  is pyramidal while  $\text{NH}_3$  is trigonal planar.  
 (1) A (2) B (3) C (4) D
26. **Assertion** :  $\text{OF}_4$  does not exists.  
**Reason** : Empty d-orbitals are absent in valence shell of oxygen.  
 (1) A (2) B (3) C (4) D
27. **Assertion** :  $\text{BeCl}_2$  shows covalent character.  
**Reason** : More polarization of  $\text{Cl}^-$  by  $\text{Be}^{+2}$ .  
 (1) A (2) B (3) C (4) D
28. **Assertion** :  $\text{MgO}$  and  $\text{NaF}$  are isomorphous  
**Reason** : Crystal structure of  $\text{MgO}$  and  $\text{NaF}$  is identical.  
 (1) A (2) B (3) C (4) D
29. **Assertion** :  $\text{NF}_3$  molecule is polar.  
**Reason** : N-F bonds are polar.  
 (1) A (2) B (3) C (4) D
30. **Assertion** :  $\text{NaCl}$  is soluble in non polar solvents.  
**Reason** :  $\text{NaCl}$  is a non-polar covalent compound.  
 (1) A (2) B (3) C (4) D
31. **Assertion** : Sigma bonds are stronger than  $\pi$  bonds.  
**Reason** : Sigma bonds are covalent bonds.  
 (1) A (2) B (3) C (4) D
32. **Assertion** :  $\text{CO}_2$  is non polar while  $\text{SO}_2$  is polar molecule.  
**Reason** : S-O bonds are polar while C-O non polar.  
 (1) A (2) B (3) C (4) D
33. **Assertion** : Both  $\text{H}_2\text{O}$  and  $\text{SnCl}_2$  are bent molecules.  
**Reason** : Both  $\text{H}_2\text{O}$  and  $\text{SnCl}_2$  are  $\text{sp}^2$  hybridised.  
 (1) A (2) B (3) C (4) D
34. **Assertion** : NO is paramagnetic in nature.  
**Reason** : Bond order of NO is 2.5.  
 (1) A (2) B (3) C (4) D
35. **Assertion** : Nitrogen is unreactive at room temperature but becomes reactive at elevated temperature (on heating or in the presence of catalysts).  
**Reason** : In nitrogen molecule, there is extensive delocalization of electrons.  
 (1) A (2) B (3) C (4) D
36. **Assertion** :  $\text{NO}_3^-$  is planar.  
**Reason** : N in  $\text{NO}_3^-$  is  $\text{sp}^2$  and no lone pair at central atom.  
 (1) A (2) B (3) C (4) D
37. **Assertion** : The electronic structure of  $\text{O}_3$  is   
**Reason** :  Structure is not allowed because octet around 'O' can not be expanded.  
 (1) A (2) B (3) C (4) D
38. **Assertion** :  $\text{LiCl}$  is predominantly a covalent compound.  
**Reason** : Electronegativity difference between 'Li' and 'Cl' is too small.  
 (1) A (2) B (3) C (4) D



39. **Assertion :-** Ozone is a powerful oxidizing agent in comparison to  $O_2$ .  
**Reason :-** Ozone is diamagnetic but  $O_2$  is paramagnetic.  
 (1) A (2) B (3) C (4) D
40. **Assertion :-**  $B_2$  molecule is diamagnetic.  
**Reason :-** The highest occupied molecular orbital is of  $\sigma$  type.  
 (1) A (2) B (3) C (4) D
41. **Assertion :-**  $BH_4^-$  is known while  $BH_6^{3-}$  is not.  
**Reason :-** B has very small atomic size.  
 (1) A (2) B (3) C (4) D
42. **Assertion :-** Some molecules are polar.  
**Reason :-** The centre of negative charge and positive charge do not coincide each other in some molecule.  
 (1) A (2) B (3) C (4) D
43. **Assertion :-**  $R_3P = O$  exists but  $R_3N = O$  does not exist.  
**Reason :-** P is more electronegative than N.  
 (1) A (2) B (3) C (4) D
44. **Assertion :-**  $ClF_3$  has T-shape structure.  
**Reason :-** It has two lone pair arrange at  $180^\circ$  (Angle).  
 (1) A (2) B (3) C (4) D
45. **Assertion :-** Bond Dissociation energy is  $F_2 > Cl_2$ .  
**Reason :-**  $Cl_2$  have more electronic repulsion than  $F_2$ .  
 (1) A (2) B (3) C (4) D
46. **Assertion :-**  $H_2O$  molecule can form four hydrogen bonds.  
**Reason :-** Two lone pairs and two hydrogens are directly attached with oxygen atoms.  
 (1) A (2) B (3) C (4) D
47. **Assertion :-** Bond angle in  is more than expected.  
**Reason :-** It is due to lp-lp repulsion.  
 (1) A (2) B (3) C (4) D

## EXERCISE-II (Assertion & Reason)

## ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	4	2	2	3	2	3	3	3	3	3	3	3	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	3	1	3	3	4	1	4	4	1	1	1	2	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	3	2	3	1	1	3	2	4	2	1	3	3	4
Que.	46	47													
Ans.	1	3													

